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SYNTHESIS OF LIQUID FUELS BY REACTING ACETYLENE OVER SOLID ACID CATALYSTS

V.M. Allenger
Hydrocarbon Processing Research Laboratory

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SUMMARY

It is proposed in this research program to study the synthesis of liquid fuels by reacting acetylene over solid acid catalysts. This research is part of a larger project at Energy, Mines and Resources Canada which has as its objective the conversion of natural gas into liquid hydrocarbon fuels, such as gasoline, by a direct process. Improvements in thermal efficiency and reductions in plant capital cost would be expected if this conversion could be carried out directly in a single- or two-stage process, in contrast to existing processes which achieve this conversion by indirect multi-stage routes. One direct process which is being considered is the pyrolysis of natural gas to acetylene and subsequent reaction of acetylene to liquid fuels. Development work in the first stage of this process, i.e., the pyrolysis of natural gas, is currently being funded by EMR. The research work described here focuses on the second stage of this direct process.

The two reactions of interest for acetylene conversion to liquid fuels are hydrogenation and polymerization. The approach adopted here is to carry out a systematic catalytic investigation with known hydrogenation and polymerization catalysts to determine what catalyst properties affect the catalyst performance in these acetylene reactions. In doing this, insight will be gained into how to modify the catalyst(s) to achieve the desired product. Three types of catalysts will be investigated - amorphous, crystalline and supported catalysts. In amorphous solids, the properties to be studied include acidity and basicity. In crystalline solids, the nature of the crystalline framework and the acidity (Si/Al ratio) will be studied. In supported catalysts, the degree of exchange and the type of cation will be examined. All the catalyst testing will be carried out in a fixed bed flow reactor at 101 kPa over the temperature range 50-500°C. A summary of these studies and the time frame to execute them are provided in the accompanying figure.

Task description and time schedule

TASK DESCRIPTION description de la tâche	TASK SCHEDULE IN MONTHS - MOIS DE LA TÂCHE EN MOIS																														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	
Process studies with a single catalyst																															
Synthesis of binary oxides																															
Testing of binary oxides																															
Synthesis of halided & alkali aluminas																															
Testing of halided & alkali aluminas																															
Procurement and preparation of zeolites																															
Process studies with a single zeolite																															
Testing of zeolites with various frameworks																															
Testing of zeolites with various Si/Al ratios																															
Synthesis of metal loaded catalysts																															
Testing of ion-exchange zeolites																															
Added hydrogen studies																															
Deactivation studies																															
Catalyst evaluation and characterization																															
Preparation of manuscripts and presentations																															

Over the course of these studies, the following contributions to knowledge are anticipated:

1. New data will be generated which will aid in designing a catalyst for converting acetylene to liquid fuels. Specifically, the performance (activity and selectivity) of amorphous binary oxides, halided and alkali oxides, crystalline binary oxides and metals supported on oxides in the polymerization/hydrogenation reactions will be determined.
2. Catalyst performance in these reactions will be correlated with the physico-chemical properties of these catalysts.

SOMMAIRE

Une étude est proposée sur la synthèse des carburants liquides par la réaction de l'acétylène sur des catalyseurs acides solides. Cette étude fait partie d'un programme de recherche au département d'Energie, Mines et Ressources Canada sur la transformation du gaz naturel aux carburants liquides par un procédé direct. Une amélioration dans l'économie thermique et une réduction dans l'investissement initial ne représentent que deux avantages d'un procédé direct à une étape en comparaison aux procédés existants indirects qui n'atteignent ce but qu'en plusieurs étapes. Un des procédés directs qui vient d'être considéré est la pyrolyse du gaz naturel en acétylène et la conversion de cet intermédiaire aux carburants liquides. La recherche sur la première étape de ce procédé, c'est-à-dire, la pyrolyse du gaz naturel est subventionnée présentement by EMR sous contrat. Cet article se converge sur le programme de recherche qui est présentement en vigueur sur la deuxième étape de ce procédé direct.

Les deux réactions qui nous concernent dans le domaine de la conversion de l'acétylène en carburants liquides sont l'hydrogénation et la polymérisation. La façon dans laquelle on propose de procéder est la suivante. Une investigation catalitique systématique sera menée avec des catalyseurs bien connus pour l'hydrogénation et pour la polymérisation d'autres réactifs avec le but de déterminer quelles propriétés des catalyseurs exercent une influence sur le pouvoir de ces catalyseurs dans les deux réactions en question de l'acétylène. Cette façon de procéder nous permettra d'apprendre comment modifier le catalyseur pour atteindre le but désiré. Trois types de catalyseurs vont être examinés, des catalyseurs amorphes, cristallins et supportés. Dans le cas des catalyseurs amorphes l'acidité et la basicité vont être étudiées. Dans le cas des catalyseurs cristallins, le rapport de silice-alumine et la nature du réseau cristallin vont être examinés. Tous les tests d'activité des catalyseurs seront réalisés en régime dynamique dans un

lit fixe sous pression atmosphérique. Les expériences seront réalisées entre 50 et 500°C sur une masse d'environ 5 g de catalyseur. La figure qui suit présente un sommaire des études proposées et du temps nécessaire pour exécuter ces études.

Au cours de ces études, on espère faire les contributions suivantes:

1. De nouvelles données expérimentales sur la conversion de l'acétylène aux carburants liquides qui aideront dans le développement d'un catalyseur à haute performance seront produites. Particulièrement l'activité et la sélectivité pour toute une gamme de catalyseurs (des solides amorphes, des solides cristallins et des catalyseurs supportés) dans l'hydrogénation et la polymérisation de l'acétylène seront déterminées.
2. L'activité et la sélectivité catalytique pour ces réactions vont être reliées aux propriétés physiques et chimiques de ces catalyseurs.

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1. INTRODUCTION

The National Energy Board (NEB)'s forecasts of supply and demand of natural gas and crude oil for 1990 indicate that Canada has a surplus of natural gas and a deficiency of liquid fossil fuel (1). Because of the lack of markets, only 71% of the available natural gas was used in 1980. Additional natural gas reserves are being found and it is estimated that these frontier supplies will not be required for domestic use before 1998. On the other hand, the supply and demand for conventional crude oil is similarly imbalanced. Canada has been a net importer of crude oil and since the demand for transportation fuels (gasoline, diesel and jet fuel) is expected to increase in the 1990's this situation will likely recur. Sufficient incentive exists therefore to look for economic and efficient routes of converting the surplus natural gas into transportation fuels. This would then make Canada self-sufficient in these commodities.

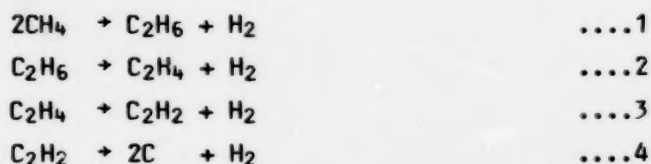
Several routes exist for the synthesis of transportation fuels from natural gas. The two commercial routes are the Fischer-Tropsch and the Mobil methanol-to-gasoline (MTG) technologies. Both routes depend on the production of synthesis gas, a mixture of carbon monoxide and hydrogen, by steam-reforming of natural gas (900°C, 2 MPa). In the conventional Fischer-Tropsch process, the synthesis gas is reacted in the presence of an iron catalyst in a fixed bed or entrained reactor (300°C, 2 MPa) (2). The reactor effluent is then cooled and fractionated to recover the desired products. The product distribution is spread over a wide range and the yield of transportation fuels depends upon the reactor and the operating conditions used (3). In the Mobil process the synthesis gas is converted to methanol over a Cu/Zn/Al₂O₃ or Cu/Zn/Cr₂O₃ catalyst (260°C, 5 MPa). Subsequent reaction of the methanol over the ZSM-5 catalyst (370°C, 0.1 MPa) yields the desired product, gasoline. It has been shown that the reforming step accounts for as much as two-thirds of the "work lost" in a methanol plant (4). The low overall thermal efficiencies of both routes, therefore, stem from the generation of the synthesis gas. Furthermore, both processes require high initial capital investments. For these reasons, it seems worthwhile investigating direct routes of liquid fuel production from natural gas.

It is theoretically and technically feasible to manufacture liquid fuels from natural gas via an alternative route, i.e., by converting the natural gas to acetylene and then polymerizing and hydrogenating the acetylene to the required fuels. Such an integrated direct process has never been carried out commercially although patents pertaining to this methodology are available (5, 6).

The first phase of an integrated route, i.e., the production of acetylene by the pyrolysis of methane, has the following three requirements:

- (i) large energy inputs
- (ii) rapid heating rate for the reactants
- (iii) rapid cooling rate for the products

These requirements are dictated by thermodynamic and kinetic considerations. Figure 1 shows the free energy of formation per carbon atom for several hydrocarbons. Details of the derived values and corresponding calculation procedures are given in Appendix A. Several points are noted in Fig. 1. At any given temperature the tendency of a reaction is from a higher curve to a lower curve ($\Delta G_f < 0$). Methane is very stable compared with other hydrocarbons at temperatures up to 1200°C. Requirement (i) above is a result of this condition. Acetylene is the only hydrocarbon whose stability is increased with temperature, however it never becomes stable with respect to its elements. The following series of reactions have been postulated for methane pyrolysis (7, 8):



The temperature dependence of reaction rate constants k_1 to k_4 is shown in Figure 2. At high temperatures, reactions 1 to 3 proceed more quickly than reaction 4. It is theoretically possible, therefore, to obtain high yields of acetylene from methane at high temperatures and short reaction times. The effect of temperature on the maximum conversion of methane to acetylene at various times of reaction is shown in Figure 3. This figure shows that a reaction time in the order of a few milliseconds is necessary to attain high acetylene yields, which explains requirements (ii) and (iii).

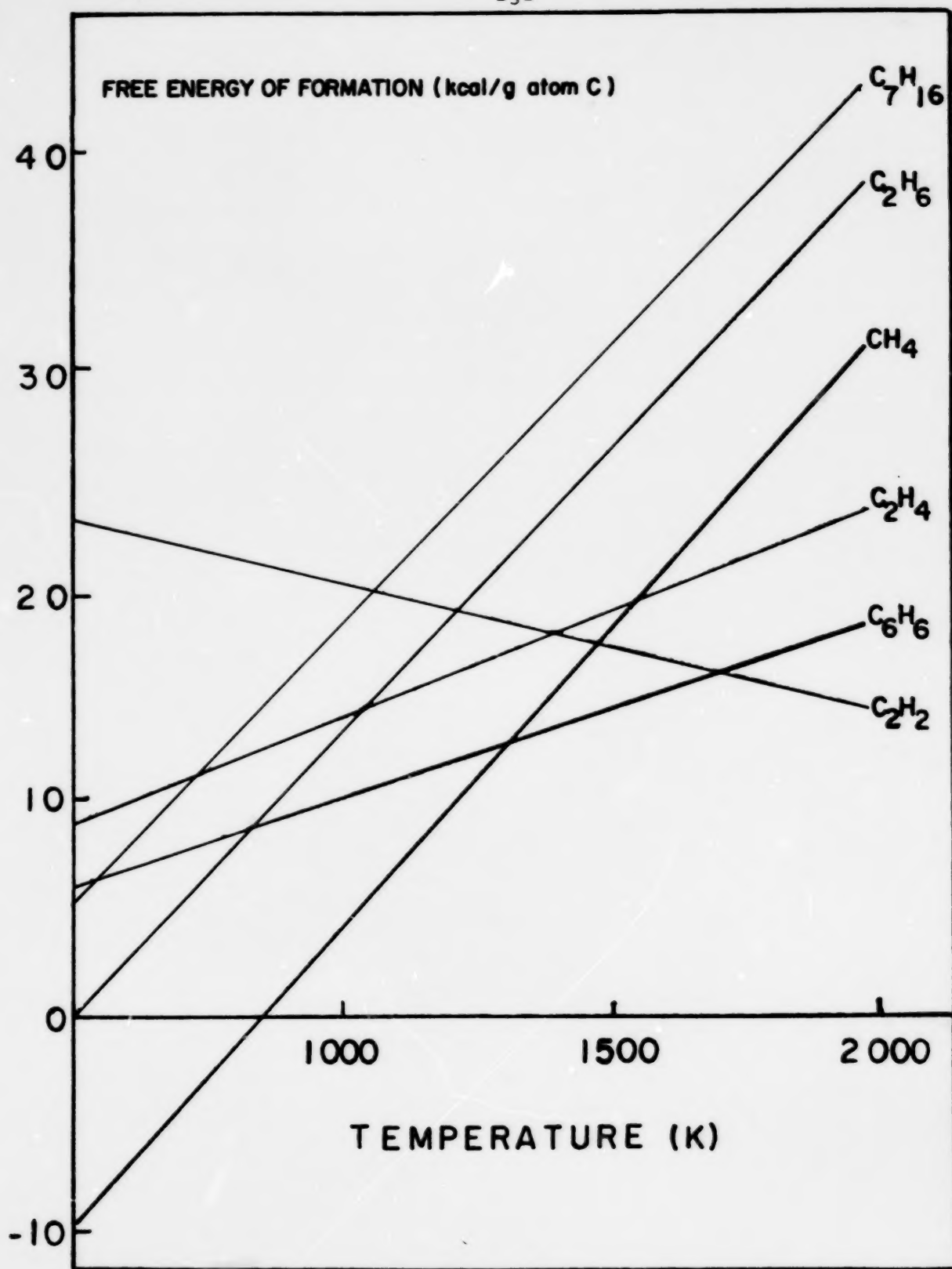


FIGURE 1
FREE ENERGY OF FORMATION OF SOME HYDROCARBONS

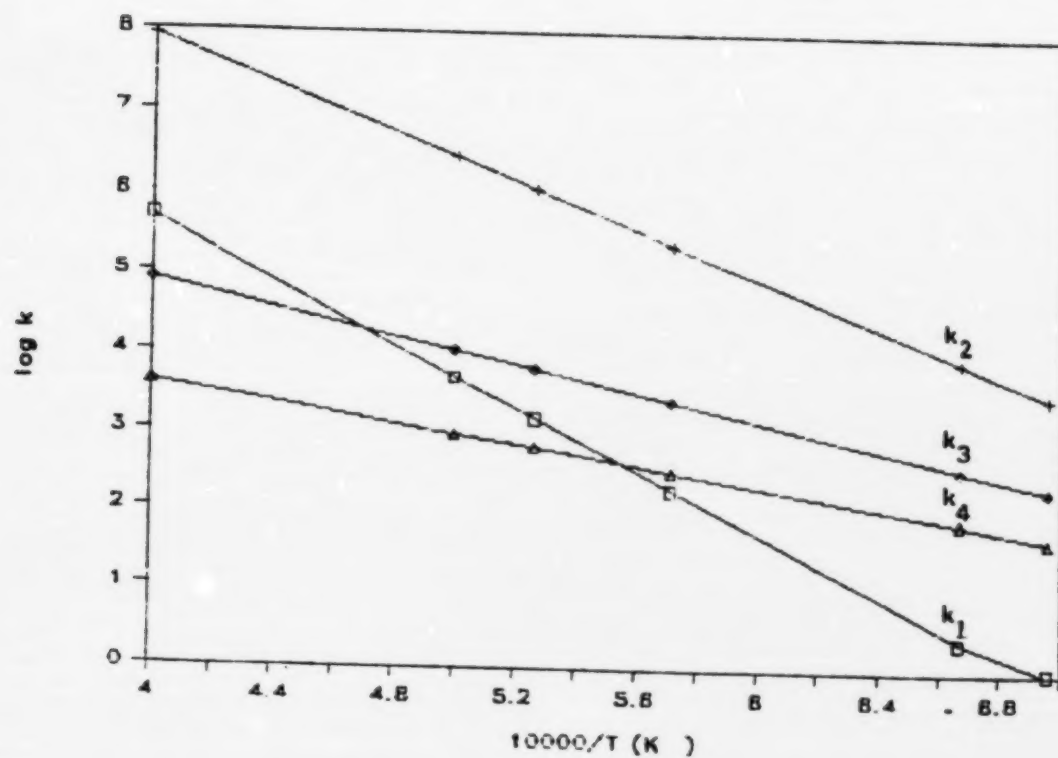


Figure 2 - Temperature dependence of reaction rate constants in the thermal decomposition of $\text{CH}_4(\text{g})$

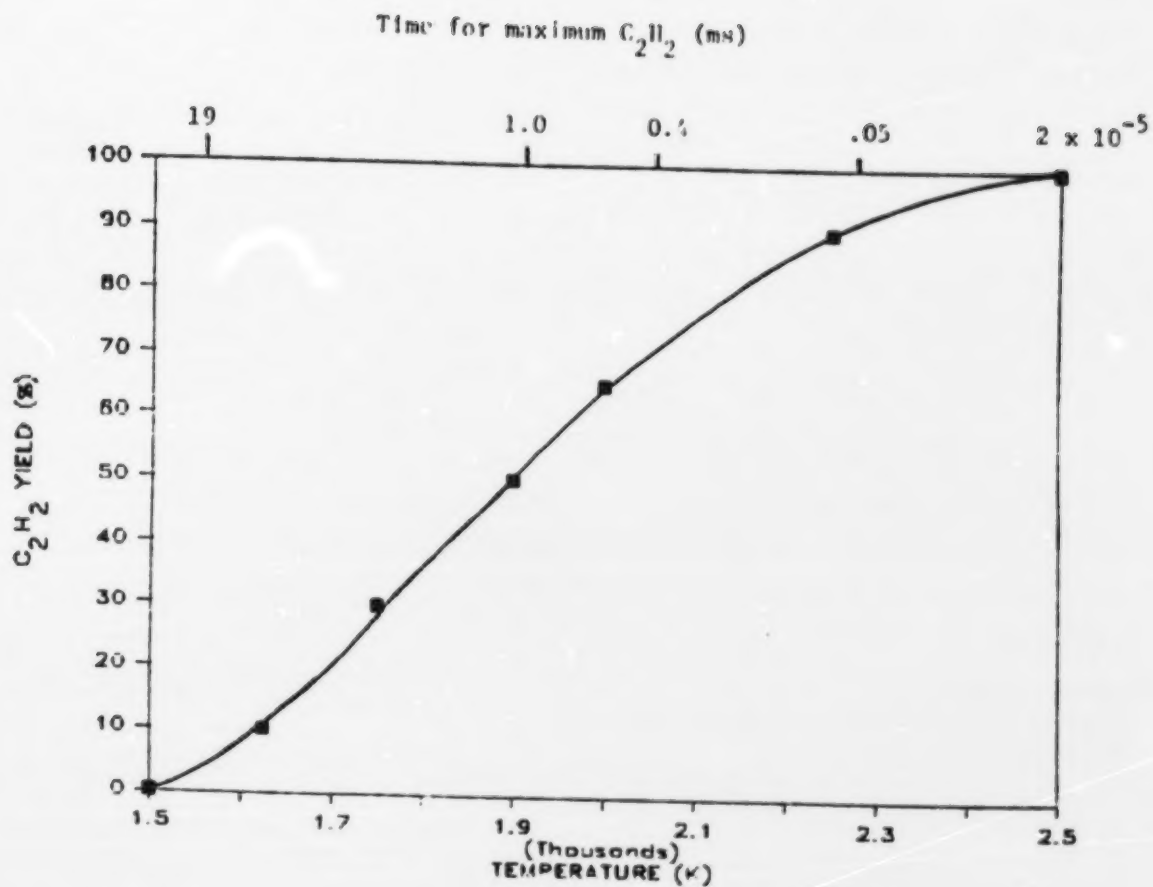


Figure 3 - Maximum conversion of methane to acetylene at various temperatures and times of the reaction (8)

Acetylene has been produced commercially by pyrolysis for many years using several techniques, namely regenerative pyrolysis, electric arc, plasma arc, partial oxidation and cracking (9-12). The partial oxidation processes are the most popular when natural gas is employed as a feed. Hydrogen is obtained as a byproduct in all these processes. Combined yields of acetylene and ethylene can reach 50% and the ethylene to acetylene ratio can be varied from 0.1 to 3 (9). Additional development work in natural gas pyrolysis to acetylene is currently being funded by Energy, Mines and Resources Canada (13).

The second phase of this direct natural gas to liquids process is the conversion of acetylene to the desired transportation fuel. It can be seen from Figure 1 that low temperatures favor the conversion of acetylene to higher hydrocarbons. Equilibrium constants for some acetylene reactions are given as a function of temperature in Figure 4. In the absence of hydrogen, two competing reactions are evident, i.e., trimerization and decomposition. Acetylene decomposition to its elements is extremely exothermic (54.1 kcal/mol). The trimerization of acetylene to benzene is similarly exothermic (48.6 kcal/mol). In the presence of hydrogen many other reactions can occur, e.g., hydrogenation and hydropolymerization.

It has long been recognized that significant yields of liquid products could be obtained by heating acetylene to below 800°C (14). Although a simple molecule, acetylene yields a sizable number of products when subjected to these temperatures. The effect of temperature on the reaction products is shown in Figure 5 for a mixture of 22% C₂H₂ in He at 101.1 kPa. The thermal polymerization of acetylene leads to complex mixtures made up largely of aromatic hydrocarbons. The production of aromatics is of particular importance because lighter aromatics, which boil in the normal gasoline range, have very high octane numbers and are therefore excellent gasoline blend stocks. Major quantities of benzene are found in these liquid products. Meyer (15) identified many more components of the liquid product, e.g., toluene, xylene, styrene, indene, naphthalene, chrysene and fluoranthene. In general, however, the thermal polymerization has not been used for synthesis mostly because many different products, including high molecular weight products, are also obtained. This disadvantage is minimized when acetylene is reacted in the presence of catalysts. Catalytic conversion of acetylene occurs at much lower temperatures and can produce quite narrow product distributions (16).

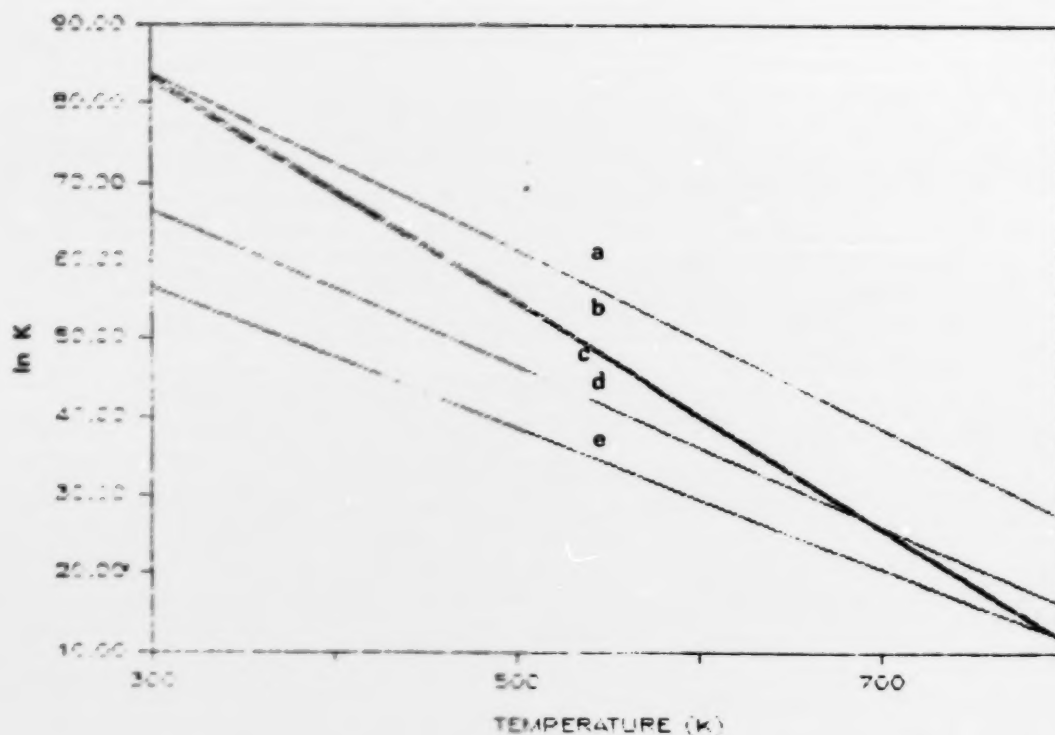


Figure 4 - Equilibrium constants as a function of temperature for the following reactions:

a	C_2H_2	$\rightleftharpoons$	$2C + H_2$	decomposition
b	$C_2H_2 + 4/3 H_2$	$\rightleftharpoons$	$1/3 C_6H_{14}$	} polymerization
c	$C_2H_2 + 6/7 H_2$	$\rightleftharpoons$	$2/7 C_7H_{16}$	
d	C_2H_2	$\rightleftharpoons$	$1/3 C_6H_6$	trimerization
e	$C_2H_2 + H_2$	$\rightleftharpoons$	C_2H_4	hydrogenation

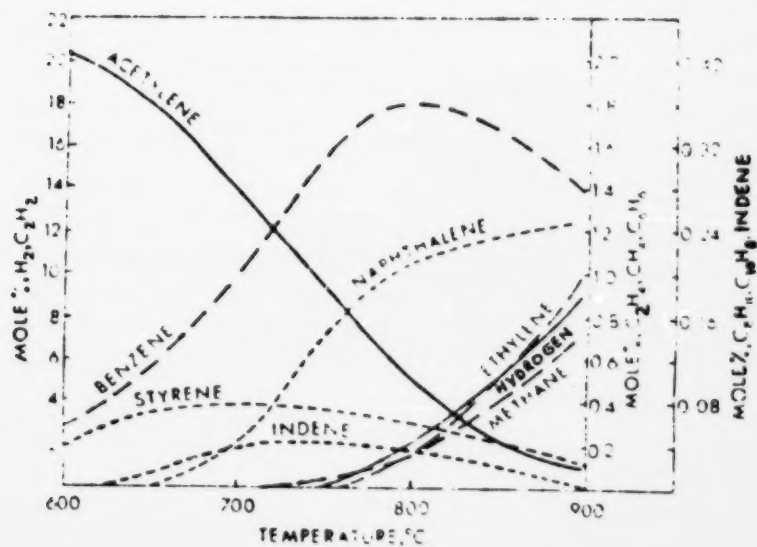


Figure 5 - Effect of temperature on the production of various hydrocarbons from C_2H_2 (8)

The reactions of acetylene have been studied extensively for the manufacture of specialty chemicals in the presence of a broad range of catalysts. These include transition metals, nickel carbonyls, carbonyls of other metals, organometallic catalysts, alumino-silicates and Ziegler-Natta catalysts. Many of these syntheses occur under very mild conditions. For example, cyclooctatetraene is synthesized using nickel carbonyl at 100°C and 1.5 MPa. In a news brief, benzene was reported to have been synthesized in a full-scale plant by the trimerization of acetylene over a chromium catalyst with 90% yield (17). There are, in comparison, very few catalytic studies on polymerization or hydropolymerization of acetylene for liquid fuel production. There is motivation for carrying out a systematic investigation of the catalytic reactions of acetylene which lead to liquid fuel.

The design and development of a catalyst is a difficult problem whether one is selecting among known catalysts or searching for new catalysts for carrying out the desired conversion. One approach is to explore the merits of catalysts used in known catalytic reactions which are believed to be analogous to the reaction in question (18). The two reactions of interest for acetylene conversion to liquid fuels are hydrogenation and polymerization. Hydrogenation catalysts include noble metals, supported metals and metal oxides. Polymerization catalysts include oxides and zeolites. Screening such a large number of catalysts represents a significant effort. In order to improve on this approach, the procedure adopted here will be to determine what catalyst properties affect the catalyst performance in these reactions. In doing this, insight will be gained into how to modify the catalyst(s) to achieve the desired goal, liquid fuels. A systematic investigation of the crystalline structure, composition (Si/Al), acidity and basicity of representative catalysts will be undertaken. This systematic study is the goal of the proposed research and is outlined in this report.

2. LITERATURE REVIEW

The literature on acetylene and the reactions of acetylene is voluminous. The two volumes by Miller (8) and the recent book by Tedeschi (9) are noteworthy in their treatments of the reactions of acetylene. Much of the early work on acetylene polymerization has been summarized in a review by Egloff (14). The two reactions of acetylene of interest in this study are catalytic hydrogenation and polymerization (which includes cyclization). The literature in these areas is discussed in subsequent sections.

2.1 HYDROGENATION

The catalysts which have been used in hydrogenation reactions are essentially those in group VIII of the periodic table, e.g., Fe, Co, Ni, Pd and Pt (20). Metals and/or supported metals catalyze this process by virtue of their ability to adsorb hydrogen (20). Other transition elements or their oxides (Cr, Mo, W, Cu, Zn) have also been found useful, however they effect hydrogenation at moderate temperatures only when high pressures are used (21).

Like the simple carbon-carbon double bond, the triple bond in acetylene can be hydrogenated in the presence of a wide variety of metals. A unique feature of the hydrogenation of acetylene is that hydrocarbons containing more than two carbon atoms are found in the products and that they sometimes constitute a major part of the products (20). This tendency of acetylene towards hydrogenative polymerization is called hydropolymerization. In the presence of hydrogen, hydrocarbon polymers are formed at temperatures substantially less than that at which acetylene polymerizes by itself, even in the presence of a catalyst. Evidence for this comes from infrared studies of acetylene adsorption on various supported metals in the presence of hydrogen and from thermal desorption studies following acetylene hydrogenation on Pt/Al₂O₃, Pt/SiO₂, Rh/SiO₂ and evaporated Pd films (21).

Bond (20) has shown that the same catalyst can be used for hydrogenation and hydropolymerization and that reaction conditions determine which reaction predominates. An increase in temperature favors hydropolymerization because the activation energy is believed to be higher than for hydrogenation. The nature and distribution of the polymers in the products of acetylene hydrogenation have been investigated using nickel on zinc chloride,

nickel-pumice and nickel-alumina as catalysts (21). The approximate distribution in terms of the carbon atoms in the polymer molecules formed over nickel-pumice in a flow system between 200 and 250°C is given in Table 1. Approximately two-thirds of the products are low boiling hydrocarbons ($n < 14$). The C_4 fraction represents a sizable yield. Since the processing of butenes to gasoline is a normal refinery practice, this fraction will be explored further. The C_4 fraction of the polymers formed in the hydrogenation of acetylene over some alumina-supported Group VIII metals has been analyzed and is shown in Table 2. The temperatures used are low, 15°C to 130°C, in order to avoid thermal reactions. The major products appear to be butenes. The distribution of the C_4 oligomers is altered substantially depending on the metal component. Iridium leads to a significant proportion of saturated product, butane. Polymerization in the presence of hydrogen seems chiefly associated with metals of smaller atomic radii (22). At comparable temperatures and gas pressures, hydropolymerization increases in the order shown:

Transition element														
Ir	≈	Pt	<	Pd	≈	Rh	<	Cu	<	Ni	<	Co	<	Fe
.126		.129		.128		.125		.117		.115		.116		.117
Atomic radii (nm)														

with iron being the most effective. This ranking provides a useful guide for selecting transition elements for bifunctional catalysts.

Some of the more recent studies on the C_4^+ oligomers formed during acetylene hydrogenation have been carried out in connection with the removal of C_2H_2 from C_2H_4 streams, therefore, the amount of C_2H_2 used in these experiments is very low (23-27). Much of the research effort has been directed at minimizing the amount of "green oil" or oligomeric products formed in C_2H_2 hydrogenation. Nevertheless, under some conditions, approximately 20% of the acetylene in these streams has been converted to C_4^+ oligomers. The C_4^+ oligomers consist of volatile products (butenes, butane, butadiene) and non-volatile products (surface polymer) at the reaction temperature. Table 3 shows the selectivity to the volatile oligomers (mostly butenes) for a variety of supported palladium catalysts (25). The zeolites with very high Si/Al ratios, e.g., silicalite and ZSM-5 exhibit the highest selectivity. The amount

Table 1 - Distribution of polymers formed in the hydrogenation of acetylene over Ni-pumice (22)

Number of carbon atoms C_n	Approximate yield (%)	Products identified in fraction
4	25	Butadiene
5	2	n-pentane, 2-methylbutane
6	25	n-hexane, 3-methylpentane, benzene
7	2	3-methylhexane
8	5	2-, 3-, 4-methylheptane
9-14	7	
15-30	17	
31- ∞	17	

Table 2 - Composition of the C₄ products (%) from acetylene hydrogenation over alumina-supported group VIII metals (initial H₂/C₂H₂ = 1) (21)

Metal	T (°C)	Butadiene	1-butene	Cis 2-butene	Trans 2-butene	Butane
Pd	17.6	trace	59.3	13.5	23.3	3.9
Rh*	13.0	0.0	42.5	34.3	7.3	7.2
Pt	135	8.3	46.5	20.3	22.1	2.8
Ir	130	0.0	35.4	17.9	1.5	45.2

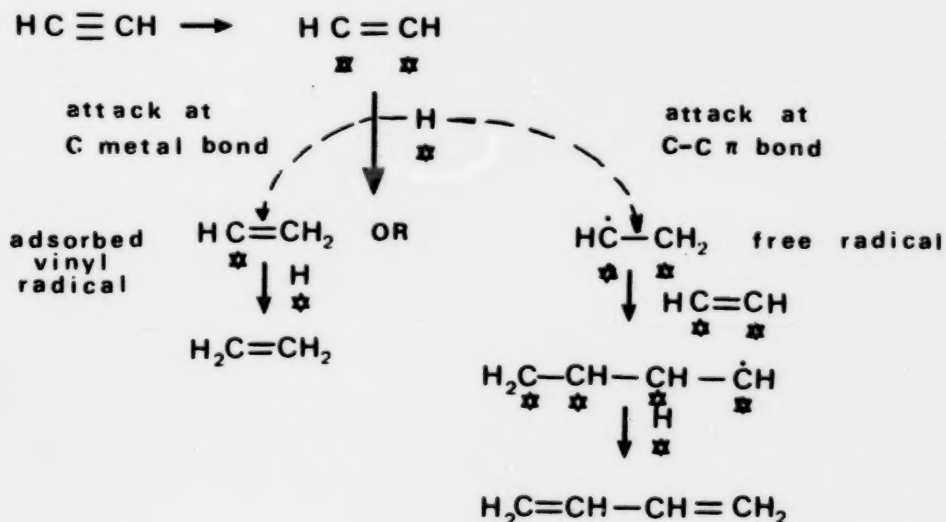
*Isobutene detected in product 8.7%

Table 3 - Average selectivities to oligomer on various catalysts at 80°C for low hydrogen feed gas (25)

Catalyst	S(oligomers)
0.031% Pd on silicalite	0.31
0.057% Pd on ZSM-5	0.23
0.033% Pd incorporated into ZSM-5	0.29
0.024% Pd on Na-Mordenite	0.13
0.040% Pd on γ -alumina	0.24

of surface polymer formed as a function of time on stream for several alumina supported Pd catalysts is given in Table 4. The amount of polymer formed shows significant variation with the support used. This suggests that the support may play a major role in the hydropolymerization process. The bifunctionality of these oxide-supported and zeolite-supported metals will be investigated as part of this research program.

Bond has proposed the following mechanism to explain polymer formation from acetylene reaction over oxide-supported Group VIII metals (20).



The first step in this mechanism is the adsorption of the acetylene molecule. Adsorption of acetylene on hydrogenation catalysts is so strong (stronger than alkanes, alkenes) that associatively adsorbed acetylene is assumed to be irreversibly adsorbed. Subsequent attack by adsorbed hydrogen leads to an adsorbed vinyl radical when a carbon-metal bond is broken and a free-radical when a carbon-carbon bond is broken. The free-radical form of the adsorbed vinyl radical is believed to initiate a vinyl polymerization process in which adsorbed acetylene molecules act as the monomeric units. Although free-radical mechanisms have been useful in describing the thermal reactions of acetylene (28), there is little, if any, experimental evidence on their suitability in describing the catalytic reactions of acetylene. Nevertheless, the adsorption of acetylene and hydrogen on the catalyst surface appears to play a major role in the reaction scheme and warrants further comment.

Table 4 - Amount of surface polymer formed in the hydrogenation of acetylene over various catalysts (26)

Catalyst	Time on stream [h]	Amount of polymer [mg polymer/gcat]	Rate of polymer formation [mg polymer/gcat/h]
A Pd/ γ -Al ₂ O ₃	12	3.68	0.30
	47	10.2	0.21
	227	36.3	0.16
B ICI 38-1	140	17.13	0.12
D Pd/ α -Al ₂ O ₃	150	6.17	0.04
F Cu/ICI 38-1	77	12.76	0.16

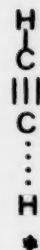
B. ICI 38-1 contained 0.04% Pd on γ -alumina

D. 0.017 wt % Pd on α -Al₂O₃

F. 95 wt % Cu ICI 38-1

Several workers have proposed the existence of two other adsorbed acetylene states:

- (1) ethylidyne complex
- (2) C_2H_x species ($x \leq 2$)



Kesmodel et al. (29) have detected the ethylidyne complex on the Pt (111) surface and have speculated that this complex is responsible for the hydrogenation of acetylene to ethane directly. Two criteria must be met for the ethylidyne species to exist, the presence of hydrogen atoms on the surface and the presence of three surface sites in a given geometrical arrangement. The third acetylene state, i.e., the C_2H_x species, is believed to be responsible for the formation of C_4 oligomers and the polymeric deposits on the catalyst surface (30). Al-Ammar et al. (30) have found that the value of x varies with the metal component, e.g. $x = 1.4$ for Pd (.128), 1.6 for Ir (.126) and 1.8 for Rh (.125) (30). The atomic radii for these elements is shown in parentheses. The fact that x varies inversely with the atomic radii of the metal may be significant. Unfortunately, no determination of the value of x has been made for transition metals with lower atomic radii, e.g., Fe and Ni, which as discussed previously have higher hydropolymerization activity. The exact nature of this C_2H_x species is not known.

It can be seen from these few studies on hydropolymerization that only the surface has been skimmed in studying polymer formation over oxide-supported metals. The effects of temperature, space velocity, pressure, metal loading, and support, among other variables, on polymer formation have not been elicited. This area will be explored further as part of this research program.

2.2 POLYMERIZATION

Polymerization of acetylene has been studied using both homogeneous and heterogeneous catalysts. The homogeneous catalysts, which are used in the liquid phase, include catalysts based on metal carbonyls (31), e.g., $\text{Ni}(\text{CO})_2$ $(\text{PPh}_3)_2$, organometallics (16), e.g., $\text{Al}(\text{C}_2\text{H}_5)_3$ and mineral acids (32), e.g., H_2SO_4 , H_3PO_4 . Carbonyls and carbonyl complexes have been used as cyclization catalysts mostly for laboratory-scale purposes and have not in general been considered for industrial use. The long list of heterogeneous catalysts includes clays and related oxide systems, e.g., activated clay alumina, activated carbon, silica gel and zeolites, e.g., Y zeolite, ZSM-5. With the exception of the organometallics, the unifying thread in all these catalysts, is the belief that the polymerization reactions in general are acid-catalyzed (33). Organometallic-catalyzed and acid-catalyzed polymerization is discussed below.

2.2.1. ORGANOMETALLIC CATALYSTS

Ziegler-Natta organometallic catalysts, which consist of titanium chlorides with aluminum and magnesium alkyls, have been widely used in the polymerization of alkenes and alkynes (16). The polymerization of acetylene in the presence of $\text{Al}(\text{C}_2\text{H}_5)_3 + \text{TiCl}_4$ at 25°C , yields 50% benzene and 24% linear polymer (16). Replacement of TiCl_4 by TiCl_3 leads to the formation of extremely unsaturated linear polymers. Similarly, if $\text{Al}(\text{C}_2\text{H}_5)_3$ is replaced by $\text{Cr}(\text{C}_2\text{H}_5)_4$ or $\text{Ti}(\text{C}_2\text{H}_5)_4$, the sole reaction product is a linear polyacetylene. Replacement of the titanium halide by VCl_4 , VOCl_3 or VCl_3 leads to the exclusive formation of benzene. Some workers have reported obtaining benzene from acetylene in up to 72% yield (16). The general feature of all these catalysts is the formation of a coordination complex bond between the π -orbitals of the acetylene and the d-orbitals of the transition metal (Ti, V) together with redistribution of electrons and the formation of new C-C bonds. The disadvantage of these homogeneous transition metal complexes as catalysts is the difficulty of handling them and separating them from the reactants. These catalysts will not be considered further in this research program.

2.2.2 ACID CATALYSTS

Polymerization reactions of unsaturated hydrocarbons are believed to be acid-catalyzed (33). The polymerization of olefins, e.g., ethylene, propylene and butylene to hydrocarbons boiling in the gasoline range has been carried out commercially using both sulphuric and phosphoric acid. To facilitate handling of these viscous mineral acids, they have been mounted or supported on inert substances such as diatomaceous earth or silica gel. Mounted phosphoric acid has been used since the 1930's to catalyze the polymerization of refinery streams (C_3 and C_4 olefins) to a gasoline fraction. Reactions catalyzed by solid acids, e.g., polymerization, cracking, isomerization exhibit features similar to reactions catalyzed by mineral acids and supported mineral acids. By analogy to solution chemistry, the primary requirement for catalytic activity in solids is that the solid be acidic. Alumina, silica-alumina and zeolites have been used as solid acid catalysts in polymerization reactions (19). Acid sites in solid catalysts may be of the Bronsted type in which it donates a proton to an unsaturated hydrocarbon or of the Lewis type in which it acts as an electron pair acceptor from a hydrocarbon. Studying the acidity of a surface consists in (1) measuring the acid strength of the various sites (not all methods distinguish between types of sites) and (2) determining how many there are (34). The techniques used to measure acidity vary and include non-aqueous titrations using Hammett indicators, infrared spectroscopy of hydroxyl groups and calorimetric determination of the differential heat of adsorption of probe molecules (NH_3 , pyridine, etc.). It is not possible in this short survey to discuss acidity and acidity measurements in detail. The reader is referred to Goldstein (34) for a complete discussion.

Much of the work on the polymerization of acetylene over solid catalysts has been carried out in the period 1900-1970. A large number of these are summarized in Tables 5 and 6. The catalysts used include sand, alumina, charcoal, silica gel, acid clay, silicon carbide and many others. Of note are the high liquid yields obtained and the significant low boiling aromatic fraction (useful fuel range hydrocarbons) of the liquid product. These studies carried out at high temperatures are not conclusive and are far from systematic. The advantage, if any, of the various packing materials used is unclear in most of this early work because of three factors. First the thermal

Table 5 - Maximum liquid yields reported from acetylene pyrolysis
(1900-1935)

Reference	Reactor	Packing	Temperature [°C]	Weight per cent C ₂ H ₂ converted to liquids	Weight per cent benzene in liquids (or benzene homologs)
Meyer (15)	Flow tube in series	-	650	60 *	20
Zelinsky (69)	Flow tube (glass)	Activated charcoal	650	70	35
Kovache & Tricot (70)	Flow tube (porcelain)	Various packings Activated charcoal	650	70	35
Ika & Ogura (71)	Flow tube (U-tube)	Coke Activated charcoal	650	70	60
Fujio (72)	Flow tube (glass, porcelain)	Japanese acid clay	650	(82)	-
Fischer et al. (73)	Flow tube (porcelain)	Silica gel	650	70	38
Haque & Wheeler (74)	Flow tube (quartz)	-	650	61	26
Berl & Hofmann (75)	Flow tube (glass)	Various packings CaO, SnO ₂ , Na ₂ SiO ₃	740	- **	30

* H₂ as co-reactant

** H₂O as co-reactant

Table 6 - Maximum liquid yields reported from acetylene pyrolysis
(1935-1970)

Reference	Reactor	Packing	Temperature [°C]	Per cent by weight C_2H_2 converted to liquids	Weight per cent benzene in liquids (or benzene homologs)
Schwarz & Bessel (76)	Flow tube *	V_2O_5 on pumice	650	22 44	66 40
Cadariu (77)	Flow tube **	Al_2O_3 , ARF ₃ , SiC graphite, C_2Ca	650	80	45
Cullis & Nettleton (78)	Static ***	Various packings Al, Fe, Zn, Cu, Ni, Carbon Kieselguhr firebrick	400	98	10
Massimilla et al. (42)	Fluidized bed+	Various packings silica sand, silica gel, graphite, activated carbon	650	85	60
Chang-Li (79)	Flow tube	Glass wool	650	44.5	64

* CO as co-reactant

** Similar products for all packings

*** IR study

+ N_2 fluidizing gas, similar products for all packings

reaction is significant in the temperature range investigated (400°C-750°C) and at these high temperatures secondary reactions play a major role in determining the product distribution. Second, the liquid analysis is simply based on boiling point cuts and definition of these is ambiguous. Third, the exothermicity of these acetylene reactions is high and isothermality in most of these tubular reactors is questionable. Massimilla et al. (42) were able to minimize the heat transfer problem in the polymerization of acetylene by using a fluidized bed reactor. They also obtained much higher liquid yields with the fluidized bed than with the fixed bed. Nevertheless, no significant improvement was effected with the various packing materials. The temperature in this investigation was 650°C and the catalytic effect may very well have been masked by thermal reactions. The factors highlighted here will be considered carefully in the present investigation.

Many more recent studies on polymerization of acetylene have been of a fundamental nature including infrared and Raman studies on alumina and zeolites and have concentrated on the formation of polyacetylene chains, i.e., linear polymers (35-39). Spectral evidence indicates that on both γ -alumina and zeolites KX, monomeric acetylene is physisorbed via its Π -electron system in a "side-on" orientation. Heaviside et al. (39) have shown that the length of the polyene chain varies with the activation temperature of the γ -alumina used, longer chain being observed at higher activation temperatures. Gravimetric results show that very little polyene (0.5 mg/g) was formed on these alumina surfaces) at room temperature. Acetylene polymerizes, nevertheless, at very low temperatures over these oxides which makes these catalysts worth investigating.

Homogeneous nickel catalysts (organonickel compounds) (31), nickel supported on silica gel ($\text{Ni}^{2+}/\text{SiO}_2$) (40) and nickel ions in NiY zeolites (41) have been shown to be active in the cyclotrimerization of acetylene at room temperatures. The conversion of acetylene to benzene occurs with close to 100% selectivity over thermally reduced Ni/SiO₂ (40). Acetylene cyclotrimerization proceeds 30-40 times more slowly on the unreduced catalyst than on the reduced catalyst. Catalyst preparation and pretreatment are important in supported metal catalysts and warrant careful consideration.

The cyclotrimerization of acetylene on NiY zeolites containing 10, 14 and 19 Ni^{2+} ions/unit cell after treatment in oxygen at 200 and 600°C was investigated by X-ray diffraction analysis, IR and EPR spectroscopies (41). The 200°C calcined samples were far less active than those treated at 600°C. These studies showed that catalyst activity depends on the number of dehydrated or partly dehydrated Ni^{2+} ions inside the supercages. Two reasons were given for this. First, C_2H_2 molecules cannot reach and complex the Ni^{2+} ions inside the hexagonal prisms. Second, the Ni^{2+} ions in the sodalite cages are inactive in the production of significant amounts of benzene since a C_6H_6 molecule cannot escape through the 2.3Å sodalite cage aperture. The Ni^{2+} population in the Y zeolite cage is roughly constant for the 600°C treated samples whereas the amount of C_6H_6 formed varies from traces (Ni-10) up to the filling of the supercages (Ni-14 and Ni-19). Furthermore, the benzene formed could be completely removed from the zeolite.

Pichat et al. (41) also showed that cyclotrimerization is not the only reaction which occurs. Other species are found in small amounts, Ni^0 and Ni^+ were detected by electron spin resonance studies. By comparison with studies of nickel supported silica, $-\text{CH}_2$ groups found were attributed to linear polymerization of acetylene on nickel metal. The amounts of Ni^0 and $-\text{CH}_2$ species increase with contact time and nickel content (41). Careful characterization of these catalyst surfaces has been shown to be very important in determining the role of the metal and of the support in these reactions and will be considered in the present investigation.

The cyclotrimerization reaction has also been studied over Cr-exchanged Y zeolites in a quartz microbalance (43, 44). At a reaction temperature of 160°C, the acetylene reaction using CrY zeolite yields only benzene. Cr (VI) has been shown to be a more active catalyst than Cr (III). At higher temperatures the reaction is less selective, with benzene, aliphatic (C_4 - C_6) and alkylaromatic hydrocarbons being obtained. Acetylene adsorption on CrY is much higher than on NaY zeolite. NaY zeolite does not show any significant activity between 70-350°C and 4 kPa. NiY zeolite (Ni-8) was tested under the same conditions at 200°C and showed similar conversions and selectivity to CrY (Cr-8). There is evidence here of some disagreement with Pichat et al. who report virtually no reaction with NiY for Ni^{2+} concentration under 10 ions/unit cell. Léglise et al. (43) suggest that, at the higher temperatures,

cyclotrimerization is limited by the zeolite structure, i.e., pore blockage by high molecular weight residue. Below 200°C, activity increases with Cr content. Above 200°C the activity becomes independent of chromium content.

In a static pyrex reactor, Légli et al. (44) studied the formation of alkylaromatics by acetylene reaction over CrY zeolites. These workers found that benzene was the major product at 350°C but toluene, ethylbenzene, xylenes and higher alkylbenzenes (and traces of naphthalene) altogether exceed benzene. In the aromatic C₈ fraction, styrene is abundant over NaY but almost absent over CrY. In addition to aromatic hydrocarbons, some aliphatics are formed over both zeolites. Vinyl acetylene is the main aliphatic in the reaction over NaY but the distribution is more diversified in the case of CrY, e.g., C₆ (C₆H₁₄ to hexadienyne), C₄ (butane to vinylacetylene), C₅ (C₅H₁₂ to C₅H₈) and C₃ (propane to propyne). The role of sodium in these reactions is not clear. Moreover, in these high conversion batch experiments secondary reactions, e.g., isomerization and alkylation, are prominent and this limits the usefulness of the information obtained.

The effect of temperature on the products and residue formed over CrY (Cr-12.9) after two hours is illustrated in Figure 6. The acetylene conversion first increases up to 150°C and then decreases from 150 to 300 but rises again at higher temperatures. Studies undertaken in a vacuum microbalance showed that the composition of the irreversibly absorbed residue was temperature dependent (44). At 70°C, the residue came off as benzene upon heating at 360°C. At 200°C, only 80% of the residue desorbed upon heating to 360°C and the products were C₃-C₆ aliphatics (36%), toluene (16%), C₈ (15%), C₉ (14%), benzene (10%) and acetylene (8%). For higher reaction temperatures (300 and 360°C) no change in mass was noted after prolonged heating but some hydrogen was evolved. This would imply that at reaction temperatures above 300°C significant secondary reactions are occurring which lead to tar formation.

Recently, investigations of acetylene reactions over ZSM-5 type catalysts have been reported (45, 46). The reactions of acetylene over these zeolites were studied by Tsai and Anderson (45) in a quartz flow microreactor containing 0.1 g of catalyst at a total pressure of 101.1 kPa and temperatures between 250-500°C. Three important results emerge from their work. First, in the absence of hydrogen in the feed, acetylene was converted with very high

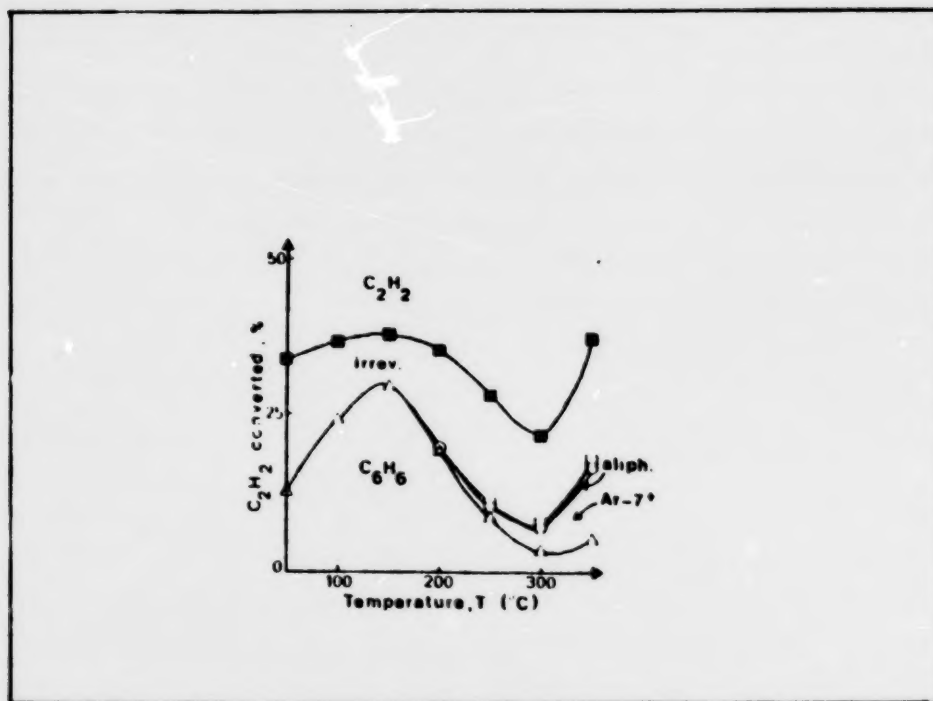


Figure 6 Effect of temperature on the products (gas desorbed) and residue formed over $\text{Cr}_{12.9}\text{Y}$. Reaction time: 2 h. (44)

selectivity to aromatics ($\approx 99\%$) in the C_6 - C_{13} range. The aromatic products in this range were always a mixture but the following main components in each class were identified: C_6 - C_8 (benzene, toluene, xylene), C_9 (methylethylbenzene, trimethylbenzene), C_{10} (naphthalene, tetralin, alkybenzenes), C_{11} (2-methyl-naphthalene), C_{12} (dimethylnaphthalene, 2 ethyl-naphthalene) and C_{13} (alkyl-naphthalenes). Second, when hydrogen was used as a coreactant, the product distribution was altered significantly in that it resulted in the conversion of a substantial fraction of acetylene to ethylene. Third, catalyst deactivation was severe in all cases and most of the activity data are given for 15 min on stream. Although the acetylene conversion at 350°C was noted to decrease from 30% to 7%, as the Si/Al ratio was varied from 25 to 436, it was not pointed out that the decrease was linear for Si/Al ratios below 240. Recently, varying the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in ZSM-5 was shown to alter the acidity of the catalyst surface (47). Higher ratios were shown to correspond to a lesser number of Bronsted acid sites. Although the conversion decreases by only 2% from a Si/Al ratio of 243 to 436, the liquid product distribution changes somewhat as seen in Figures 7 and 8. A shift to lower molecular weight products is evidenced as the Si/Al ratio is increased. Acetylene conversion increased with temperature (250 - 500°C) from 4.3% to 38.2%, however, space velocity was increased simultaneously with reaction temperature in these experiments. At higher space velocities the conversion decreases therefore the effect of temperature on conversion is likely to be greater than reported. Furthermore, at 400 and 500°C , thermal conversion of acetylene is expected yet no blank reactions were reported. Catalyst deactivation increased with increasing time on stream. The product distribution shifted to larger quantities of C_{10} - C_{13} aromatics with longer times on stream.

The use of Fe replacing Al in the ZSM-5 framework has recently been disclosed in the patent literature (47). Table 7 summarizes some examples of acetylene conversion from the patent. If it is assumed that all the conversions and product distributions are reported for 15 min on stream, then it appears that the presence of iron drastically alters the activity and the product distribution of the ZSM-5 catalyst. A discussion however would be speculative because of the scanty description given in the patent.

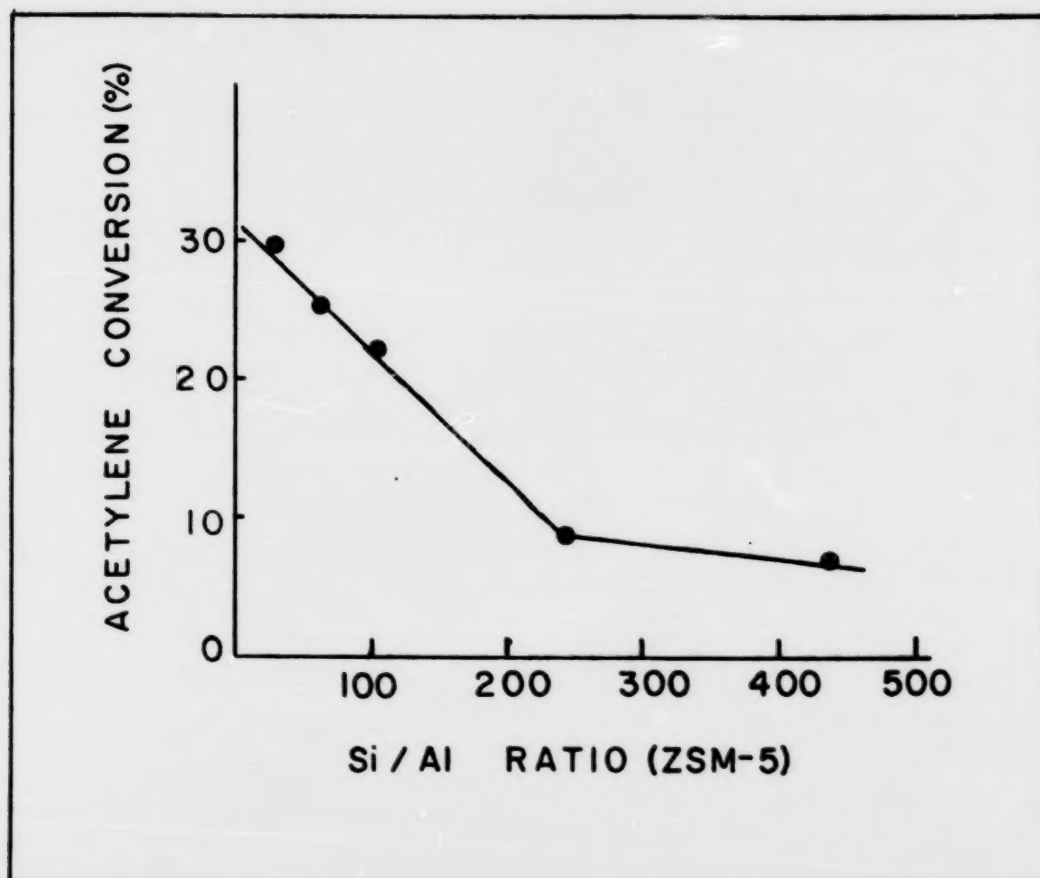


FIGURE 7 Acetylene conversion as a function of the Si / Al ratio in ZSM-5 (45).

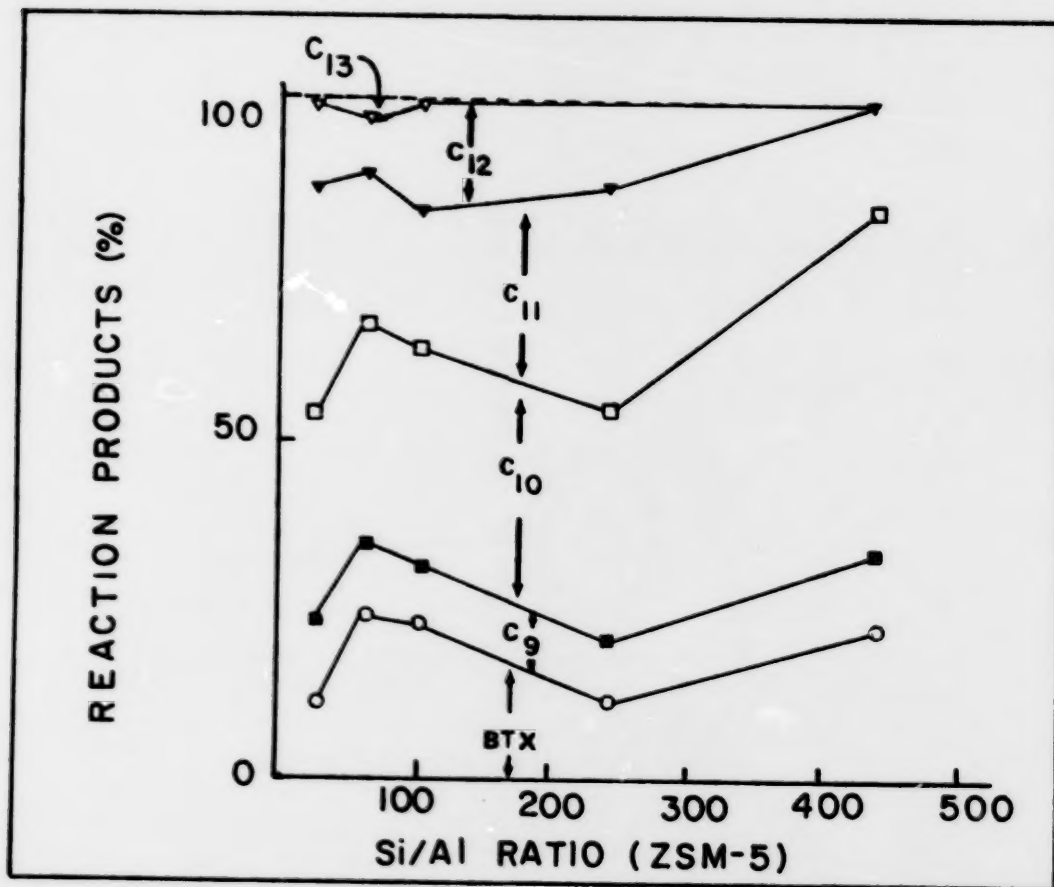
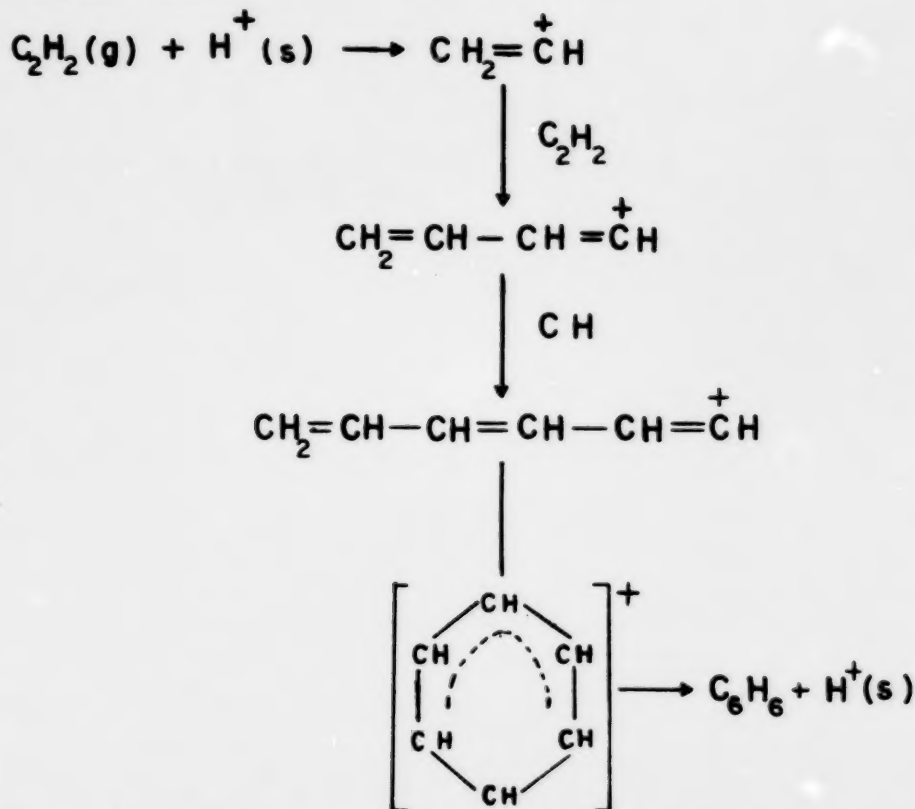


FIGURE 8 Product distribution in the conversion of acetylene to liquids over ZSM-5(45).

Table 7 - Acetylene conversion to liquids over ZSM-5 (46)

Example	14	19	23
Feed C_2H_2 (cc/min)	0.5	0.5	0.4
H_2	-	1.0	2.2
He/ N_2	2.9	6.0	3.0
Catalyst	H-ZSM-5	H-ZSM-5	Fe-ZSM-5
SiO_2/Al_2O_3	120	120	140
Temperature ($^{\circ}C$)	400	400	400
Conversion % C_2H_2	45.1	35.5	86.9
MHSV (h^{-1}) C_2H_2	0.4	0.4	0.3
Products (%) Non-aromatics	11.3	13.1	4.4
BTX	60.4	55.5	30.6
C9	10.5	25.2	10.7
C ₁₀ ⁺	17.9	6.1	54.3

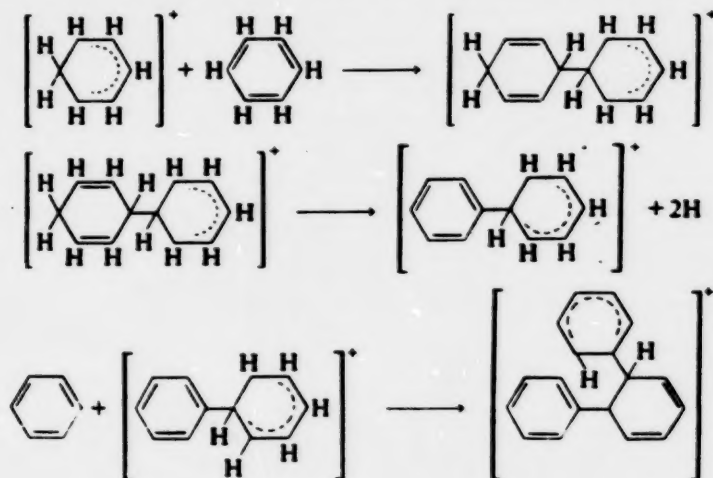
Tsai and Anderson (45) have proposed the following mechanism for the reaction of acetylene over ZSM-5:



The polymerization is proposed to proceed via a vinyl cation intermediate. The concept of the vinyl cation appears to explain the aromatic products found and is consistent with the carbonium ion theory of acid-catalyzed reactions. However, reactions between the vinyl cation and $\text{H}_2(\text{g})$ suggested by these workers to explain the non-aromatic products found is extremely speculative.

The amount of acidity and acid-strength distribution have been shown to vary with the nature of the cation present, the degree of exchange and the heat treatment (48, 49). Partial poisoning of the acid sites in ZSM-5 by Na exchange (54% exchange) was shown to cause a 50% reduction in acetylene conversion (45). A significant shift to higher molecular weight products in the product distribution was also noticed for the polymerization reaction. This may imply that even weak acid sites are active in secondary, tar forming reactions.

The vinyl cation mechanism would imply considerable coke formation, since once aromatics are present, they can react to give higher-molecular-weight hydrocarbons and coke, which are believed to be formed by condensations and by combination of aromatics with other aromatics as coke. The formation of coke from benzene is illustrated by the following reaction sequences (50):



The interest that recent workers have shown in zeolites as acetylene polymerization catalysts may stem from the following observations on acid-catalyzed reactions (51):

- (1) the rate of formation of coke is lower in zeolites than in their amorphous counterparts,
 - (2) the coking tendency changes with variations in structural constraints.
- It has been demonstrated with zeolite ZSM-5 that alkylaromatics once formed cannot react further (by cyclization, dehydrogenation or further alkylation) and lead to coke deposition because of the smaller dimensions of the zeolite channels (51). In the MTG process, the catalyst has low coking activity and the coke which is formed is believed to be deposited for the most part on the outer surface. The exterior area of zeolite crystals is only about 1% of the total, but if diffusion limitations are significant, it becomes necessary to poison or inactivate exterior sites so they do not contribute excessively to the reaction (19).

Tsai and Anderson (45) compared catalyst deactivation on ZSM-5 for two Si/Al ratios (25 and 60). Less coking occurred with the zeolite having the higher Si/Al ratio (presumably the lower acidity). This appears to be

consistent with cracking reactions where very high acid strengths, either zeolite X, zeolite Y or silica-alumina lead to excessive formation of coke. Unfortunately deactivation studies for a much higher Si/Al ratio were not reported thus no conclusions can be made as to the effect of Si/Al ratio and acidity on catalyst deactivation. Limited work has been done on deactivation in ZSM-5 and other zeolites. Since catalyst deactivation is an important feature of these acetylene reactions, more work is warranted in this area.

It is evident from the studies cited that more experimental work is required in order to understand acetylene polymerization and the role of the catalyst in assisting polymerization. Some catalyst properties intimately related to this reaction which have emerged from this discussion include acidity, crystallinity, nature of the cation and the degree of exchange. Exploring the relationship between catalyst performance in this reaction and these catalyst properties is a goal of the present research.

3. PROGRAM OBJECTIVES

The brief discussion in the previous section summarizing the existing literature on acetylene conversion to liquids has identified a large number of catalyst properties which affect polymerization including hydropolymerization.

The scope of the present investigation is to elicit the relationships between some of these catalyst properties and catalyst performance in the reactions of interest. The specific objectives of this research program are described in detail in sections 3.1 to 3.5.

3.1 ROLE OF PROCESS VARIABLES

One of the major objectives of this study is to obtain quantitative information regarding activity and selectivity of various catalysts in acetylene polymerization/hydropolymerization. Two problems must be addressed in order to meet this objective. First, a suitable reactor must be designed and constructed and second provision must be made for analysis of the gaseous, liquid and solid products.

A detailed description of the continuous flow tubular reactor and the product analysis system which will be used in this study is provided in the experimental program. As noted earlier, both hydrogenation and polymerization have large heats of reaction. With fast exothermic reactions, one must be concerned with the elimination of large temperature gradients between catalyst particles, in the gas film surrounding the catalyst and inside the catalyst particle. Axial temperature gradients have been minimized by inserting the tubular reactor in a metal block which is heated by a 3-zone resistance furnace. The use of an inert diluent in the reacting mixture further assists in attaining isothermality. Calculations based on a number of theoretical criteria will be made to determine the extent of the temperature gradients across the gas film and within the catalyst particle (Appendix B). The results of these calculations, based on some preliminary experiments, will determine to some extent the catalyst particle size, the partial pressures and the total pressure used in the present study.

The process variables in this study include the reaction temperature (40-250°C), the residence time (0-5 s), the reactant partial pressures ($P_{C_2H_2}$, P_{H_2} , P_{CH_4}) and the catalyst particle size. Because of equipment limitations, the absolute pressure range is narrow (130-200 kPa) and will not

be considered an operating variable. Approximately 25 catalysts are to be investigated in this study. A complete investigation of each catalyst with respect to the process variables would require a very large number of experiments. Since the catalysts can be divided into two main categories, i.e., amorphous and crystalline, checks on both pore and film diffusion limitations will be carried out for a representative catalyst from each group. Similarly, the effect of the process variables on catalyst performance will be determined for one member from each group. It is assumed here that similar behaviors within catalyst groups will be found so that appropriate operating conditions can be chosen from these tests on the representative catalysts. A central composite experimental design will be used to determine the effect of linear velocity (residence time), reactant partial pressure and temperature on catalyst performance and requires a total of 14 different experiments and at least one repeated experiment at the centre point of the design. A discussion of optimal catalyst performance is given in section 4.1.

3.2 ROLE OF SURFACE ACIDITY

Alumina (Al_2O_3) has been used extensively as a solid acid catalyst and catalyst support (19). Pure alumina may exhibit acid properties depending on the nature of the heat treatments and resulting changes in structure (19). The acid strength of alumina may be deliberately increased by incorporation of halogen ions such as chloride and fluoride (52-54). Fluorination has been shown to enhance the polymerization of olefins and of conjugated dienes (52). Fluorine has also been used as a promoter in co-polymerization (53). Increases in activity occur at low fluorine contents, typically 1%-6% wt F (54). In order to investigate the role of surface acidity, a series of catalysts will be prepared which have various fluorine loadings ($\text{F}/\text{Al} = 1/20, 1/10, 1/5$) and therefore acidity. The activity of these fluorided aluminas will be correlated with fluoride loading.

Unlike alumina, pure silica exhibits no acidic character. Mixtures of silica and alumina however have seen wide use in acid-catalyzed reactions, e.g., polymerization, cracking (19). Binary mixtures of these oxides exhibit high acid strengths. With silica-alumina essentially all the acid sites are strong. Good correlations exist between the acidity of the amorphous

silica-alumina (which is a function of composition and heat-treatment) and the activity for polymerization of ethylene and propylene (19). A number of correlations have also been reported between catalytic activity and type of acid site. In this study, we hope to establish similar correlations for acetylene hydropolymerization.

Other binary metal oxides such as $\text{SiO}_2\text{-ZrO}_2$, $\text{Al}_2\text{O}_3\text{-Bi}_2\text{O}_3$ are also known to show acidic character and have been used as acid catalysts (55-57). Tanabe and coworkers (57) have advanced a hypothesis which explains the mechanism of the formation of acid sites in binary oxides and predicts whether the acid sites will be of the Bronsted or Lewis type. The hypothesis applies to a case where a small amount of a metal oxide (guest) is introduced into a matrix metal oxide (host). The portion of a guest is considered to be about 1-10 atomic %. According to the hypothesis, the acid site is formed by an excess of negative or positive charge in a model structure of a binary oxide. The sign and magnitude of the charge are determined by the coordination numbers and valences of the positive and negative elements in the model structures. The model structure is pictured according to the following two postulates:

1. The coordination number of a positive element of the host metal oxide and that of the guest metal oxide are maintained even when mixed.
2. The coordination number of a negative element (oxygen) of a major component oxide (host) is retained for all the oxygens in a binary oxide.

Lewis acidity is expected to appear upon the presence of an excess of the positive charge and Bronsted acidity is assumed in the case of an excess of a negative charge. This hypothesis has been applied to Al_2O_3 based catalysts. The acidity of binary oxides, containing Al_2O_3 as a host oxide, which is predicted by the hypothesis is summarized in Table 8. Details of these calculations are provided in Appendix C. The series of amorphous binary metal oxides shown in Table 8 will be synthesized, with alumina as the major component (58,59). The activity and selectivity of these catalysts in acetylene polymerization will be determined.

Alkali metals are frequently used as poisons when using Al_2O_3 as a catalyst or support in an effort to eliminate secondary reactions and obtain the primary product distribution. This poisoning of the active acid sites of alumina by alkali ions, e.g., Na and K, has been noted by many authors (19,

Table 8 - Calculated acidities of various binary oxides

Component		New acid site type		Average electronegativity	Mean acidity
Major	Minor	Bronsted	Lewis		
Al ₂ O ₃	MgO	-1	-	8.25	4.5
	TiO ₂	-	+1	12	-4
	SiO ₂	-	+2	13.4	-6.3
	P ₂ O ₅	-	+2	16.8	-11

* molar ratio = 1

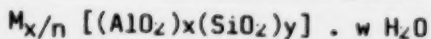
60). The effect of these poisons on the product distribution in the acetylene polymerization reactions will be investigated by varying the alkali metal, Na and K at two metal loadings ($\text{Na/Al} = 1/10, 2/10$).

In summary, the following objectives have been set to explore the role of surface acidity:

1. To investigate the influence of increased acid strength on catalyst performance by varying the F/Al ratio in a series of amorphous alumina catalysts.
2. To investigate the influence of acid site type (Bronsted or Lewis) on catalyst performance by varying the minor component oxide in binary oxide catalysts having alumina as the major oxide component.
3. To investigate the effect of decreasing the number of acid sites on catalyst performance by varying the loading and type of alkali poison.

3.3 ROLE OF CRYSTALLINE FRAMEWORK AND DEALUMINATION

Zeolites are highly crystalline, hydrated aluminosilicates that upon dehydration develop a uniform pore structure having minimum channel diameters of about 0.3 to 1.0 nm. The size depends primarily upon the type of zeolite and secondarily upon the cations present and the nature of treatments such as calcination and leaching. The pore structure for selected zeolites is given in Table 9. The structural formula of zeolites is given by:



The metal cation (of valence n) is present to produce electrical neutrality since for each aluminum tetrahedron in the lattice there is an overall charge of -1 . Zeolites are often prepared in the sodium form but the sodium ion can be exchanged for various other cations, e.g., H^+ to form more active zeolites for carbonium-ion hydrocarbon reactions. Zeolites in general exhibit higher catalytic activities for acid-catalyzed reactions, e.g., hydrocracking than their amorphous counterparts. This increase in activity is not primarily an acidic effect since it has been shown that the amorphous silica-aluminas and HY zeolites are of similar acidity (61). The success of these crystalline materials for various acid-catalyzed reactions such as cracking and isomerization is based on their shape selectivity (51).

Table 9 - Pore structure of selected zeolites (19, 51)

Zeolite type	Name	Void fraction from H ₂ O content	Channel geometry	Kinetic diameter of dehydrated form	SiO ₂ /Al ₂ O ₃ ratio
SMALL PORE	Linde Type A	0.47	0.42nm, 30	0.36-0.39 nm	
	Erionite (M ⁺) ₄₅ Al ₉ Si ₂₇ O ₇₂ 27H ₂ O	0.35	0.36x0.52, 30 tortuous	0.43	16
MEDIUM PORE	ZSM-5 Na ₇ Al ₇ Si ₉₆ -n ₀ 192 16H ₂ O		0.54x.56 1D 0.51x.55 1D		20-400
	ZSM-11 Na ₇ Al ₇ Si ₉₆ -n ₀ 192 16H ₂ O		0.51x.55 3D		20-400
LARGE PORE	Mordenite Na ₈ Al ₈ Si ₄₀ O ₉₆ 24H ₂ O	0.28	0.67x0.7, 1D interconnecting	0.62	15 (10-100)
	Linde Type X	0.5	.74, 30	0.81	2.5
	Linde Type Y (M ⁺) ₂₉ Al ₅₈ Si ₁₃₄ O ₃₈₄ 24H ₂ O	0.48	.74, 30	0.81	5

In order to examine the effect of this shape selectivity in the polymerization reactions of acetylene, zeolites with different cage structures will be tested, e.g., small pore Linde Type A, medium pore ZSM-5 and large pore Linde Type X. A relationship will be established between the product distribution in acetylene polymerization over these catalysts and the catalyst effective pore structure.

Mordenite differs from the other naturally occurring aluminosilicate zeolites, in that the extent to which alumina can be removed from the structure without altering significantly the crystallinity of the material is great. Mordenite normally has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of about 10. However by various dealumination techniques, this ratio can be progressively increased to the point where nearly all the alumina is removed (62). Catalytic activity of aluminum-deficient mordenite depends upon the preparation method, the degree of aluminum removal, the acidity and the effective pore diameter (48, 49). Acid dealumination usually generates a more active material than the parent zeolite. Moderate dealumination generally increases activity or leaves it unchanged, while advanced dealumination leads to a decrease in activity. Progressive dealumination also tends to decrease the total acidity of the zeolite while modifying the acid strength distribution. Highly dealuminated zeolites show a decline in catalytic activity, due in part to the drastic reduction in total acidity of the zeolite. Acid dealumination also alters the pore geometry and increases the effective pore diameter, thus reducing resistance to diffusivity. This feature has been shown to affect the deactivation rate of highly dealuminated zeolites in various cracking reactions. By analogy, the catalytic properties of the high-silica synthetic zeolite ZSM-5 may be affected by this aluminum deficiency, although less is known about these catalysts. In order to investigate the effect of zeolite dealumination on catalyst performance (activity and selectivity) in these acetylene reactions carefully characterized samples of ZSM-5 with various Si/Al ratios will be tested ($\text{Si/Al} = 30, 60, 100, 200$).

In summary, therefore, the following objectives have been set to explore the role of the crystalline structure:

1. To investigate the influence of the crystalline framework on catalyst performance by testing zeolites having different cage structures (and effective pore diameters).

2. To investigate the influence of dealumination on catalyst performance, zeolites with varying Si/Al ratios will be prepared and tested.

3.4 ROLE OF BIFUNCTIONALITY

Bifunctional catalysts which have the dual function of assisting hydrogenation and polymerization may be obtained by the addition of a hydrogenating component, usually a metal as discussed earlier. Incorporation of a metal component can be made in both amorphous and crystalline catalysts. Fluorinated noble metal-supported catalysts are widely used in reforming processes. Pt-alumina mainly catalyzes the dehydrogenation reaction, F-alumina catalyzes the isomerization reaction and Pt-F-alumina has been found to effectively catalyze both reactions (53). Bifunctional catalysts have been shown to retard coking and aging by pore blocking due to coke deposition. The two functions polymerization and hydrogenation may also be possible and may lead to different reaction sites and ultimately to desired reaction products.

As we have seen in the literature review, limited information exists on bifunctional catalysts to achieve polymerization and hydrogenation of acetylene. The order of reactivity of various metals/supported metals in acetylene hydropolymerization presented in section 2.1 showed that metals with smaller atomic radii exhibited higher activity. Chromium and nickel on zeolite Y have been tested as acetylene polymerization catalysts, albeit not in the presence of hydrogen. As noted earlier, polymerization over zeolite ZSM-5 in the presence of hydrogen (cf no hydrogen) leads to a decrease in catalyst deactivation and a significant shift in product distribution to non-aromatics. With Fe supported on ZSM-5 and with H_2 and H_2O as coreactants a significant portion of the product was aromatic (C_{10}^+). This picture of the role of bifunctional catalysts is incomplete at best.

In order to study the role of the hydrogenative component, i.e., the metal ions in assisting polymerization, the following objectives have been identified:

1. To investigate the influence of Group VIII metal ions on the performance of acetylene polymerization catalysts, a series of catalysts will be prepared by dispersing different metal ions, e.g., Fe, Co, Ni, Pd to the same level

on a zeolite support. This zeolite support will be determined after evaluation of the experiments described in the previous section.

2. To investigate the influence of hydrogen on catalyst performance (activity, selectivity, deactivation) the catalysts prepared above will be tested with hydrogen as a coreactant at different H_2/C_2H_2 ratios ($H_2/C_2H_2 = 1, 0.5, 0.25$).

3.5 ROLE OF CATALYST DECAY

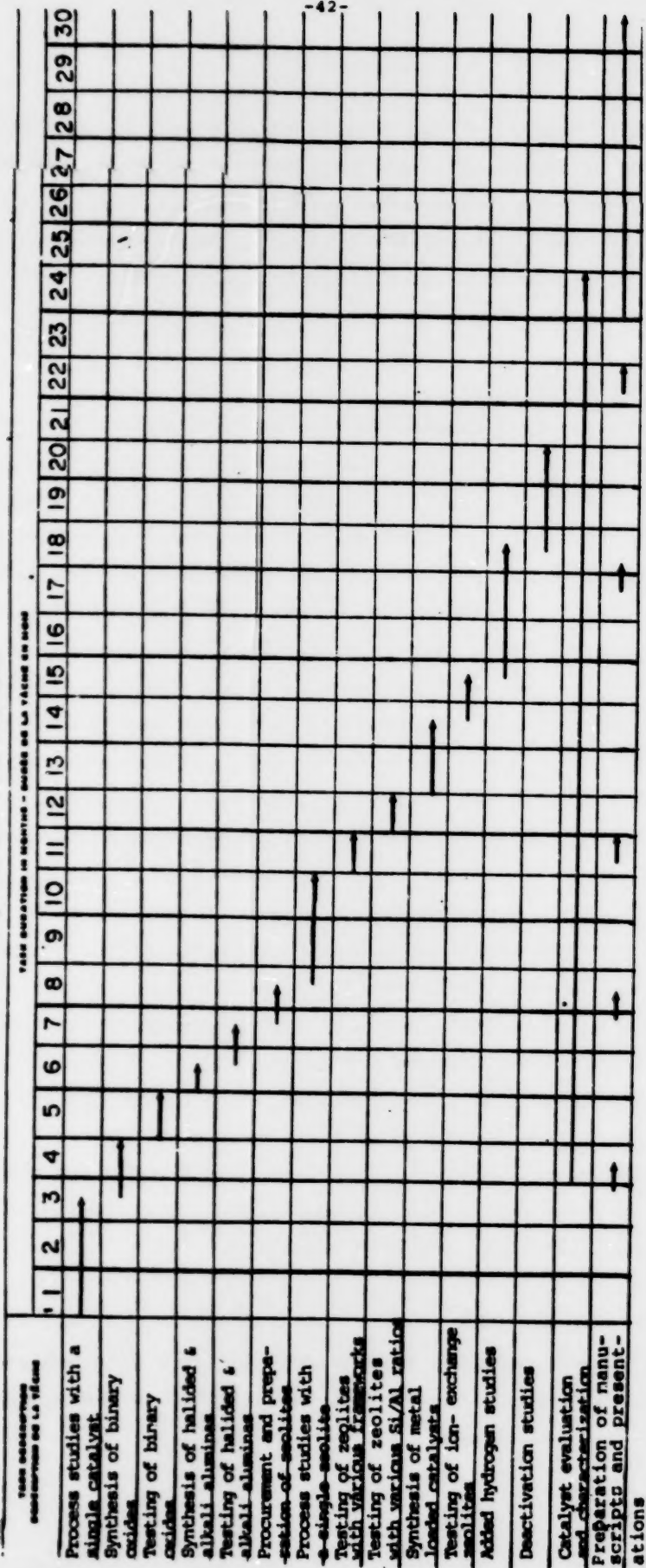
All the catalysts discussed so far, whether amorphous or crystalline, exhibit severe deactivation under conditions of hydrogenation and/or polymerization of acetylene. This catalyst deactivation is not uncommon to other hydrocarbon systems. Although catalyst deactivation has been attributed to a large number of factors, one of the major contributors is the buildup of carbonaceous species (residues) on the catalyst surface. Despite its importance, limited information is available on the quantity and type of residues formed over various catalysts in these acetylene reactions. In order to gain some insight into the problem of catalyst decay, one of the objectives of this investigation is to study the behavior of selected catalysts with time on stream. This can be achieved in several ways. For the purposes of this study, the rate of coking will be determined by using a microbalance where the carbon deposited on the catalyst can be measured as a function of time. In addition, a temperature programmed pyrolysis (in inert gas) of these carbonaceous residues and a chromatograph analysis of the gas phase products will be carried out every minute.

Catalyst aging has been characterized by decay models (63). Most models use empirical power laws because the coking rate is a complex function of temperature, space velocity, and the time the catalyst has been exposed to the reacting mixture. An expression of the type $C = At^n$, where C is the weight per cent carbon on the catalyst, t is time, and A and n are constants, will be used here. This expression has been successful in modelling zeolite and SiO_2/Al_2O_3 deactivation in cracking reactions.

3.6 CRITICAL PATH SCHEDULE

A detailed work schedule is provided in Figure 9 to achieve the objectives outlined in sections 3.1 to 3.5. The tasks listed in the schedule can be grouped into five main areas:

FIGURE 9
Task description and time schedule



1. Catalyst preparation
2. Catalyst characterization
3. Catalyst testing
4. Catalyst evaluation
5. Reporting

Each of the items 1 through 4 will be covered in somewhat more detail under the experimental program. It will be noted that a minimum of 30 months is estimated to complete the work described in this report.

4. EXPERIMENTAL PROGRAM

4.1 CATALYST PREPARATION

The catalysts to be screened in this study can be divided into two categories - amorphous and crystalline. The amorphous catalysts include fluorinated and alkali alumina and binary oxides with alumina as the major component. These amorphous catalysts will be prepared according to known methods such as impregnation and coprecipitation (64, 65). The starting material (support) for all these catalysts is alpha alumina monohydrate (catapal SB from Conco, Peterboro, NJ). The zeolite catalysts will be purchased from catalyst manufacturers. Group VIII metals will be incorporated into these zeolites by known ion exchange or impregnation methods (48, 49). Table 10 summarizes the materials and the methods which will be used in this study.

4.2 CATALYST CHARACTERIZATION

Emphasis has been placed on correlating catalyst behavior (performance) with the physico-chemical properties of the catalyst. Physical and chemical catalyst characterization therefore constitutes an integral part of this research program. Table 11 outlines the characterization techniques which will be used in the present study.

In order to compare different catalysts or the effects of various treatments on catalyst performance, it is necessary to know the extent to which a change in activity is caused by a change in the surface area of a catalyst, in contrast to a change in the intrinsic reactivity. For this reason, measurements will be made of the internal pore surface area, the total volume of the pores and the pore size distribution. The bulk chemical composition of all the catalysts will be determined by atomic absorption.

To supplement these analyses, surface analytical methods, e.g., ESCA (electron spectroscopy for chemical analysis), AES (Auger electron spectroscopy), X-ray diffraction crystallography and infrared spectroscopy will be used to further understand the effect of various catalyst modifications on the catalyst performance. ESCA (also called XPS, X-ray photoelectron spectroscopy) is a powerful technique which can analyze all the elements except hydrogen and helium. The technique involves measuring the energies of electrons ejected from an atom when it is irradiated with monochromatic X-rays. The photoelectrons are emitted with a kinetic energy, E_k , which is equal to

Table 10 - Catalyst starting materials and preparatory methods

Catalyst	Starting material	Method
F/alumina	NH ₄ F	Wet impregnation
Alkali/alumina	NaOH, KOH	Wet impregnation
<u>Binary Oxides</u>		
MgO - Al ₂ O ₃	Mg(NO ₃) ₂ ·6H ₂ O	Wet impregnation
P ₂ O ₅ - Al ₂ O ₃	NH ₄ H ₂ PO ₄	Wet impregnation
SiO ₂ - Al ₂ O ₃	Harshaw Filtrol Corp Al-1609	
TiO ₂ - Al ₂ O ₃	TiCl ₄ , AlCl ₃	Co-precipitation
<u>Zeolites</u>		
MS Type 4A	Union Carbide U.S.A.	
ZSM-5	Mobil Oil U.S.A.	
MS Type 13X	Union Carbide U.S.A.	
<u>Supported Metals</u>		
	Co(NO ₃) ₂ , Ni(NO ₃) ₂	Ion exchange
	Fe(NO ₃) ₃ , Cr(NO ₃) ₃	
	H ₂ Pt Cl ₆	

Table 11 - Characterization techniques of physical and chemical properties of catalysts

Property	Method	Equipment
Chemical composition	ESCA/SAM X-ray fluorescence directly coupled plasma ion chromatography	PHI 548 & 600 SPECTROMETERS ARTEC EEDS II BECKMAN SPECTRASPAN IV DIONEX 2000
CHN	Combustion	PERKIN ELMER ELEMENTAL ANALYZER
Surface area (m^2/g) (pore size distribution)	N_2 adsorption	CARLO ERBA STRUMENTATIONE SORPTOMATIC 2000
Pore volume (cm^3/g) (pore size distribution)	Hg porosimetry	MICROMERITICS AUTOPORE 9200
Crystal structure (crystallite size)	X-ray diffraction	
Surface acidity	IR spectroscopy	NICOLET FOURIER TRANSFORM SPECTROMETER

the difference between the X-ray photon energy, $h\nu$, and the electron binding energy, E_b . Depending on the binding energy, both valence electrons and core electrons may be emitted. The binding energies of the core electrons are characteristic of a particular element. Since the irradiating X-ray energy is fixed, an accurate measurement of the photoelectron kinetic energies provides a means of element identification. It is also possible to distinguish elemental oxidation states and other structural effects by shifts in binding energy. This technique will be used to determine the surface and bulk fluorine loading in the fluorinated alumina catalysts as well as to determine the presence of AlF_3 both before and after reaction. XPS will also be used to study catalyst deactivation and in some cases to follow changes in metal dispersion.

Electron vacancies created by irradiating a sample with monochromatic X-rays can be filled up immediately by other electrons (relaxation). The energy set free by the relaxation process is released in the form of characteristic X-rays (which is the basis of X-ray fluorescence spectroscopy) or is transferred to another electron which is then ejected. This last electron, the so-called Auger electron, has a kinetic energy which depends on the energy of all electron levels involved in the process. The energy of this Auger electron is independent of the energy of the source radiation by which the primary hole was created and it is characteristic of the type of atom which was excited and can therefore be used for element identification. Auger electron spectroscopy normally employs an electron beam as source radiation. This electron beam can be highly focused allowing high spatial resolution surface element identifications at specific sample locations ($\ll 1.0$ micron); line scans and imaging are also therefore possible. This is done using Scanning Auger Microscopy (SAM). ESCA and SAM allow detection to levels above 0.1 atomic per cent. Furthermore, shifts in the kinetic energy may be used to indicate, for example, whether phosphorus is present in the form of phosphite or phosphate. In the case of supported metal catalysts, this technique will be used to determine the extent to which the element exists as an oxide in contrast to an aluminate.

X-ray diffraction crystallography may be used to obtain information about the structure and composition of crystalline materials (66). The minimum limit of detection is approximately 5% for compounds and 1% for elements. The mean crystallite size of a material can also be determined from the broadening of an X-ray diffraction peak. The line broadening is inversely proportional to crystallite size and can be used to give the microcrystalline size in the range of about 3 to 10 nm. This technique will be used here to ascertain the crystallinity of the various zeolite catalysts before and after the metal deposition.

4.3 CATALYST TESTING

An experimental system has been constructed and assembled for testing the various solid catalysts. The experimental system consists of an inlet gas purification and delivery manifold, a fixed bed tubular reactor and the analytical equipment as shown in Figure 10. Each of these is discussed briefly.

Inlet Gas Manifold

Nitrogen (99.99%) supplied by Air Products is fed via two-stage pressure regulator through a Linde low pressure gas purifier and an oxygen trap to a Matheson mass flowmeter. Atomic absorption grade acetylene supplied by Canadian Liquid Air, 99.5% stated purity, is dissolved in acetone in the gas cylinder. Purification is carried out in three stages. The acetylene gas is passed through a cold trap (160°C) where most of the acetone vapor is condensed, then it is bubbled through a concentrated sulphuric acid bath (98%) for further acetone removal and finally it passes over an activated charcoal trap for trace acetone removal. The acetylene stream is sampled and checked for acetone content using a Kitigawa detection tube before and after each experiment. The purified acetylene stream is metered with a Matheson mass flowmeter. Mixtures of acetylene in nitrogen are prepared by having both gases flow at the required rate into a mixing chamber filled with Berl saddles. From the exit of the mixing chamber, the gas mixture is sent to the reactor.

Reactor and heater

The experiments will be carried out in a continuous flow reactor at 6 psig and from 200-800°C. The catalyst charge can be varied from 1-10 g and is centred in an annular quartz reaction tube 1 cm ID x 55 cm in length containing a centred stainless steel thermowell (.375 cm OD). Heating is supplied by a three-zone resistance furnace made by wrapping heating coils around a 5 cm OD stainless steel block 1 cm thick. The control thermocouples for the three zones are located on the exterior surface of the stainless steel block. Seven thermocouples along the coaxial thermowell permit the measurement of axial temperature profiles during an experiment. Isothermality has been achieved over a 5 inch section $\pm 1^\circ\text{C}$. Quartz chips and quartz wool are used to separate the inert quartz packing from catalyst. The pressure drop in the reactor bed is calculated to be 2 psi at the most. (See Appendix D.)

Product Analysis

A liquid tracer (n-undecane) is injected via a Sage Model 355 syringe pump into the effluent gas as it exits the reactor. This tracer is needed to obtain quantitative analysis of the liquid products using a flame ionization detector. The product stream then flows through a heated 16-port Valco

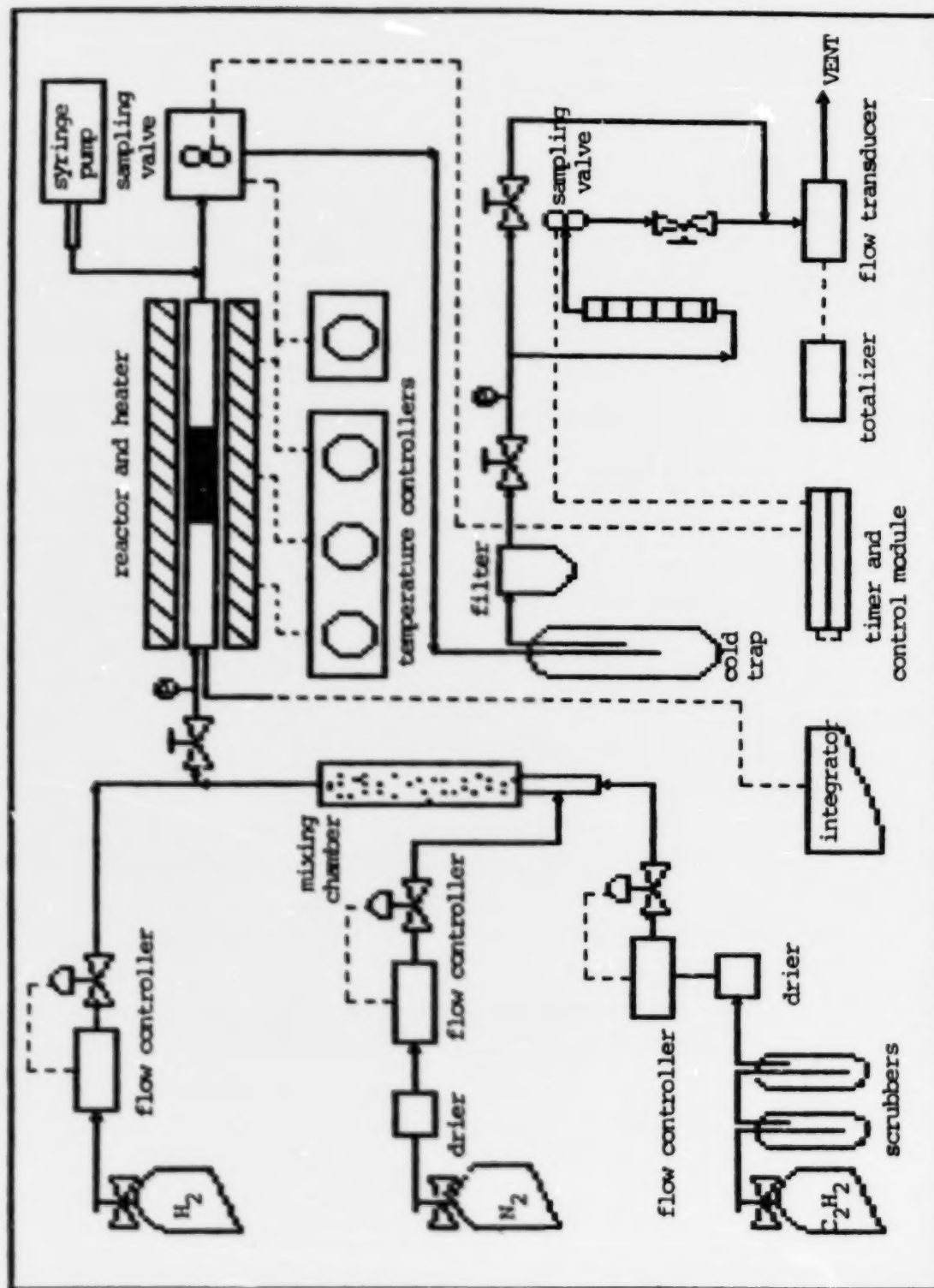


FIGURE 10 EXPERIMENTAL SYSTEM

sampling valve where at regular intervals the valve position is switched and a product gas sample is stored for later analysis. At the exit of the gas sampling valve the product stream is immediately cooled in a dry ice-acetone bath to condense the liquid products, e.g., n-undecane, benzene, toluene, naphthalene etc. The uncondensed materials including unreacted acetylene, nitrogen and uncondensed reaction products, e.g., C_2H_4 , CH_4 , n-butane are sent to a second sixteen-port gas sampling valve where again at regular intervals the valve position is switched and a gas sample is stored for subsequent gas analysis. This exit gas is monitored with a Matheson mass flow meter and a totalizer and later vented. Pressure is varied with a back-pressure regulator and total pressure is monitored using a Viatron pressure transducer.

Gas analysis is carried out using a Carle AGC 111 Series S gas chromatograph equipped with a thermal conductivity detector. This chromatograph is specially configured (columns and micro valve switching) for natural gas analysis, e.g., alkanes C_1 - C_5 , alkenes C_2 - C_5 , C_2H_2 . A Spectra-Physics 4270 integrator is used to measure peak areas and retention times. Details may be found in Figure 11. A typical gas chromatogram is provided in Figure 12.

Vapor analysis, i.e., condensible products kept in the gas phase by heating the Valco 16-port valve is carried out using a Varian Vista 6000 chromatograph equipped with two FID detectors and with capillary and packed column options. A Spectra Physics 4270 integrator is used to measure peak areas and retention times. A 0.25 mm ID, 0.25 μ m film DB-5 capillary column 30 m in length is used for trace analysis. A Chromosorb W-HP 80/100 mesh column impregnated with 5% OV-101, 1.8 m in length and 3.1 mm O.D. is used for routine analysis. Automation of this analysis system is shown in Figure 13. The approximate retention times and response areas for sample calibration compounds are listed in Table 12.

The liquid product from the cold trap is recovered and a simulated distillation on a Hewlett Packard 5880A Series Gas Chromatograph with a 0.5 m stainless steel column filled with 10% VC-W982 on Chromosorb PAW is carried out. Product identification is carried out occasionally using GC-MS.

4.4 CATALYST EVALUATION

Characterization of catalytic activity, selectivity and decay for the reactions being studied requires useful and representative measures for these

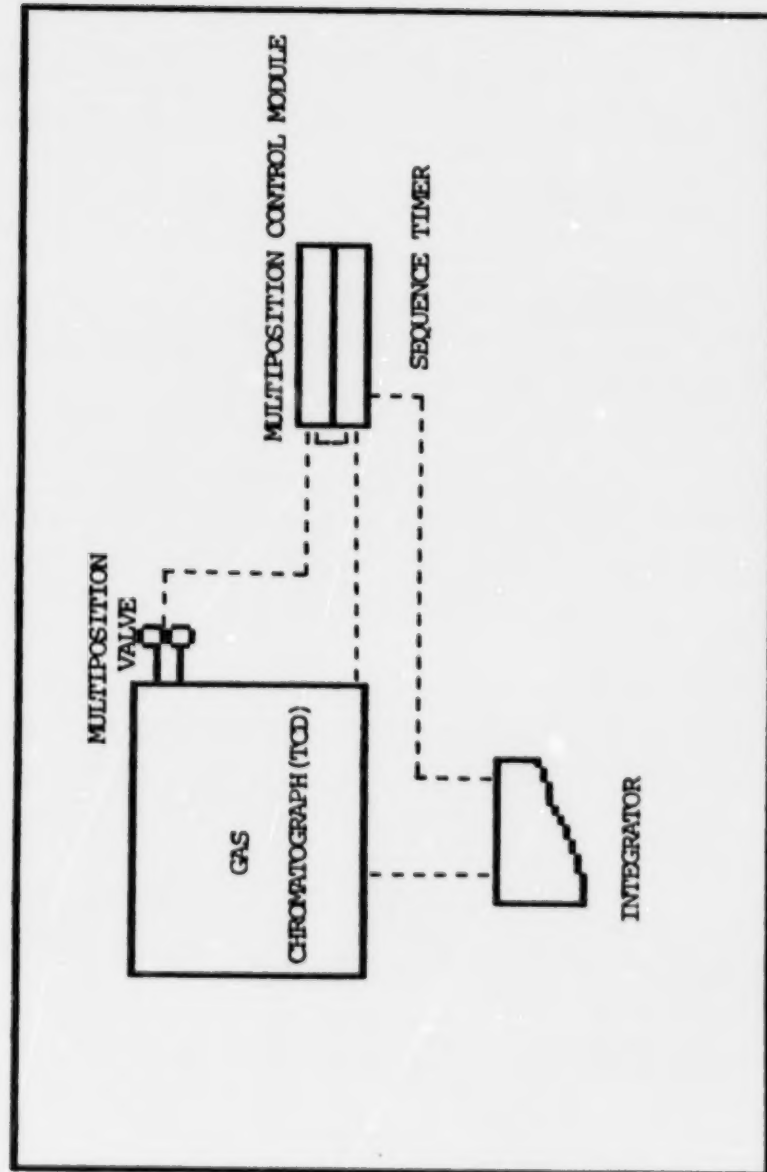


FIGURE II Gas chromatograph configuration with thermal conductivity detector

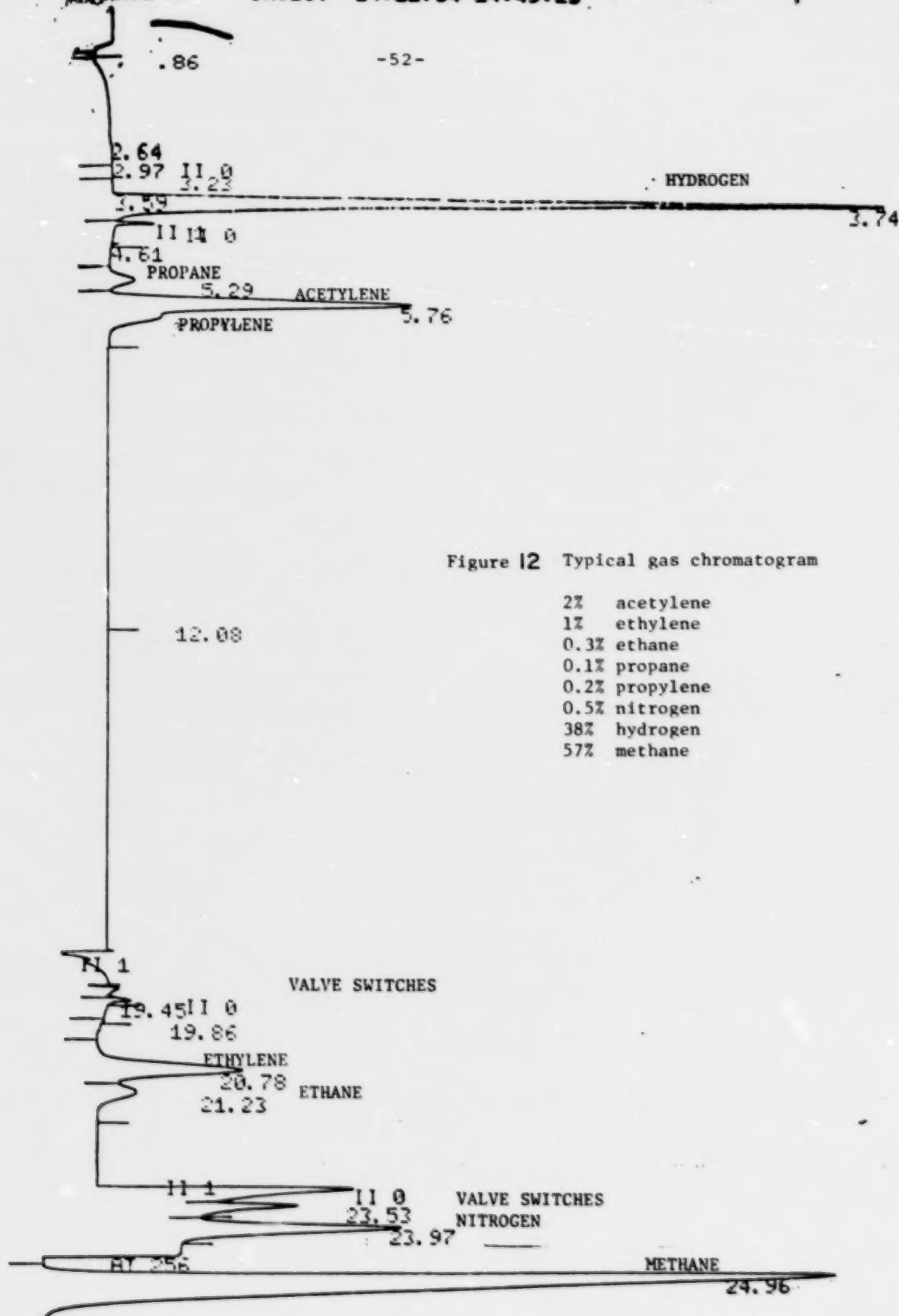
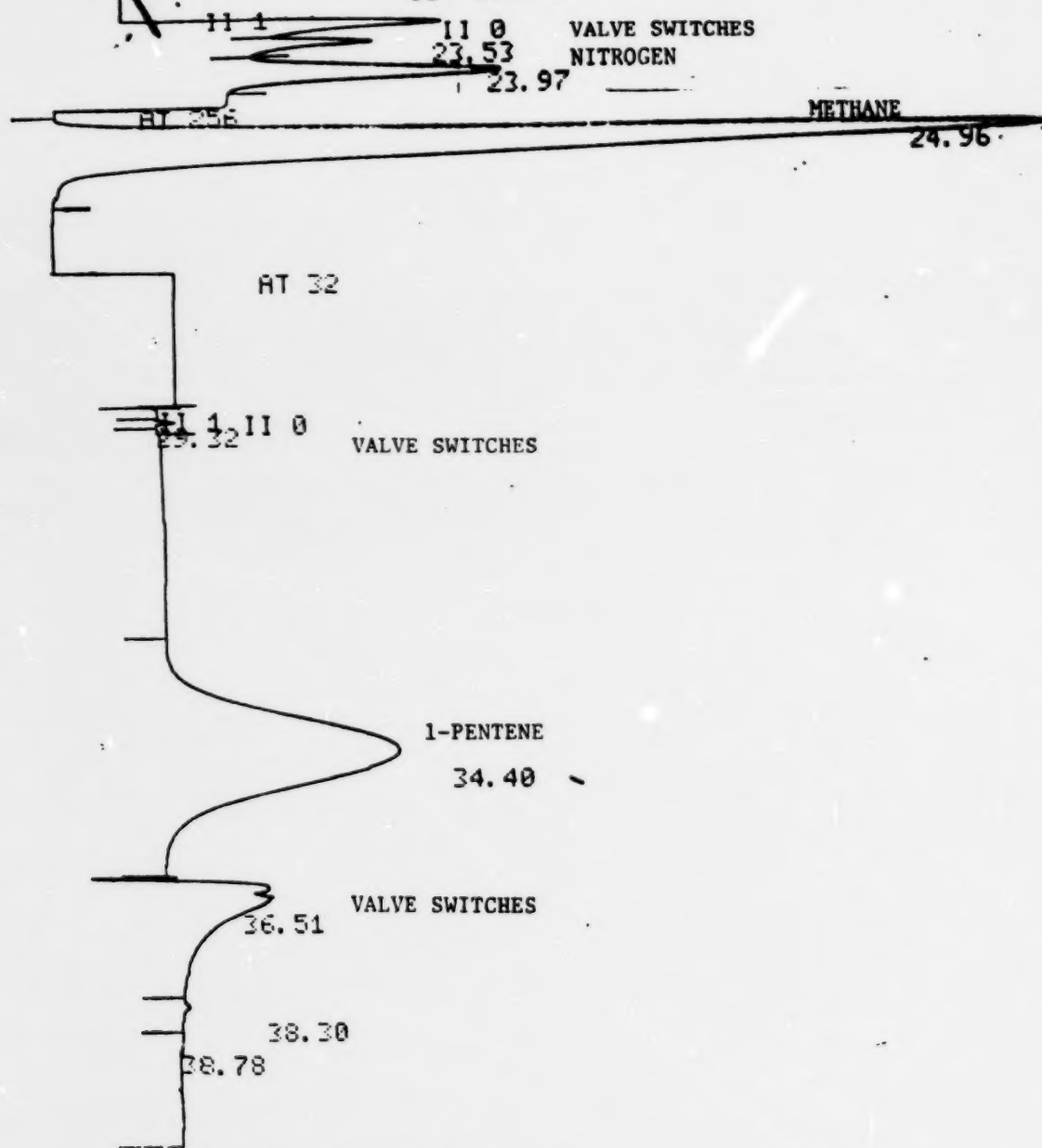


Figure 12 Typical gas chromatogram

2% acetylene
 1% ethylene
 0.3% ethane
 0.1% propane
 0.2% propylene
 0.5% nitrogen
 38% hydrogen
 57% methane

-52- cont'd-



END OF CHROMATOGRAM (40 min)

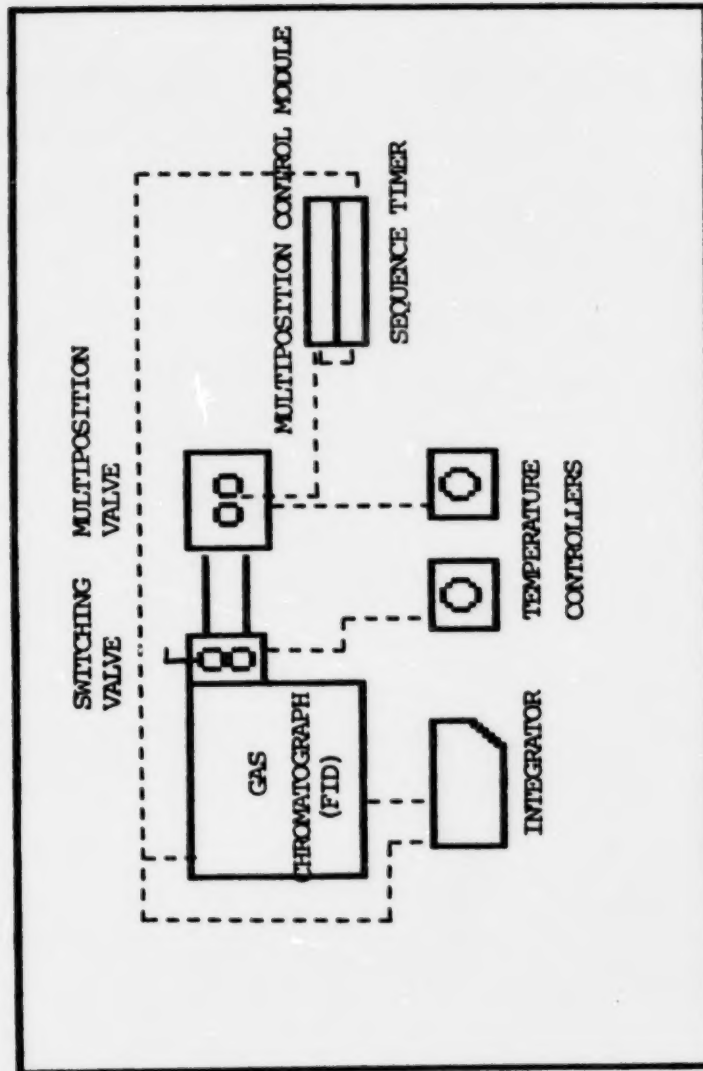


FIGURE 13 Gas chromatograph configuration with flame ionization detector

Table 12 - Approximate retention times and response areas for calibration compounds

Compound	Retention Time [min]	Response Area ¹
Benzene	1.12	120731
Toluene	1.99	156262
o-Xylene	3.79	18289 (*)
m-Xylene	3.73	128573
p-Xylene	3.74	176198
Ethylbenzene	3.52	220261
Cumene	4.94	304435
Mesitylene	6.16	438439
p-Cymene	7.86	238439
n-propylbenzene	5.77	264543
n-Butylbenzene	8.37	3498 (*)
n-Undecane	11.6	285954
n-Hexyl Benzene	15.44	48524 (*)
n-Octyl Benzene	21.85	42310 (*)
n-Decyl Benzene	27.81	207004

¹ All sample sizes are 0.01 μ L, 10^{-12} FID sensitivity
* These samples will be rerun to ascertain discrepancy.

performance criteria. Activity, in this study will be expressed in terms of the total conversion of acetylene, i.e., conversion of acetylene to all products:

$$X = (C^{\circ} - C)/C^{\circ}$$

where C° is the concentration of acetylene at the reactor inlet (mol/L), C is the concentration of acetylene (mol/L) at the reactor outlet and X is the fractional conversion.

When more than one product is obtained as is the case here, then the selectivity of the catalyst, which refers to the ratio of the yield of one product to the yield of a second becomes important. The selectivity can be determined, therefore, by measuring the yields of the components of interest as shown below:

$$Y(i) = \frac{y_i F}{(x^{\circ} F^{\circ} - x F)} \quad ; \quad Y(j) = \frac{x_j F}{(x^{\circ} F^{\circ} - x F)}$$

where Y = yield of liquid vapor component i or of gaseous component j

y_i = mole fraction of component i in vapor stream

x_j = mole fraction of component j in gas stream

F = flow rate of product stream (mL/min)

F° = flow rate of feed stream (mL/min)

x° = mole fraction acetylene in feed stream

x = mole fraction acetylene in product stream

The data analysis procedure used to obtain these yields is described in detail in Appendix E. The selectivity to liquids (s) can be calculated as shown below:

$$S = \frac{\sum_{i=1}^m y_i F}{\sum_{j=1}^n x_j F} = \frac{\text{Total liquid product}}{\text{Total gas product}}$$

where m is the total number of vapor components and n is the total number of gaseous components. A number of other selectivity ratios can also be defined. In this study the selectivity to C_n oligomers (liquids) where $n > 4$ are of interest. For the purposes of this study, these simple definitions will be used.

5. CONTRIBUTIONS TO KNOWLEDGE

In the course of this research program, the following contributions to existing knowledge are anticipated:

1. New data will be generated which will aid in designing a catalyst for converting acetylene to liquid fuels. Specifically, the performance (activity, selectivity and decay) of:

- (1) amorphous binary oxides
- (2) halided and alkali oxides
- (3) crystalline binary oxides

and (4) metals supported on oxides

for polymerization/hydropolymerization reactions will be determined.

2. Catalyst performance in these reactions will be correlated with the physico-chemical properties of these catalysts. These properties include:

- (1) surface acidity in binary oxides
- (2) surface acidity in halided and alkali oxides
- (3) pore structure of crystalline oxides
- (4) Si/Al ratio (acidity) in crystalline oxides
- (5) charge/radius ratio of metals in crystalline oxides

6. SUMMARY OF INITIAL PROGRESS

In the first phase of this project, the pyrolysis of methane was studied at high temperatures (900-1100°C). These studies confirmed the pioneering work in this area carried out in the early part of this century. Liquid yields from direct pyrolysis were found to be extremely low. The results of these studies were presented at the 34th Canadian Chemical Engineering Conference in Québec City in Oct. 1984 (67). Searching for a catalyst which would operate at these high temperatures appeared to be a challenging but highly speculative enterprise. Subsequently, alternate approaches to the manufacture of liquid fuels from natural gas were reviewed and evaluated. Liquid fuel synthesis via acetylene emerged as a viable route.

In the second phase of this project, routes for converting acetylene to liquid fuels were examined. Two options have emerged here. The first option consists in hydrogenating the acetylene to ethylene and subsequently oligomerizing the ethylene to α -olefins which can be isomerized to the desired fuel. Although the technology for the different processing steps in this option is available, it has not been commercially proven as an integrated process (68). The second option which has been presented in this report in some detail is the hydrogenation/polymerization of acetylene directly to liquid fuels. This option requires more research and development before it can be considered a proven technology.

The design, construction and assembly of a bench-scale system for carrying out catalyst screening for the acetylene reactions of interest has been completed. Several problems were encountered in the process and the resulting solutions are incorporated into the experimental system described in section 4. Preliminary experiments have been carried out in order to debug the experimental equipment.

Several catalysts have been synthesized and partially characterized. Some of these are presented in Table 13. The fluorided alumina catalysts were prepared by impregnating the alumina support with an aqueous solution of NH_4F of the appropriate concentration. Additional distilled water was added to obtain a mixture suitable for extrusion. The catalyst extrudates were dried in air at 105°C for 8 h and calcined at 450°C or 1000°C for 8 h in air. After calcination, the catalysts were analyzed for fluorine content by ESCA.

Table 13 - Physical and chemical properties of some catalysts

Catalyst property	Catalyst number			
	MB 204	MB 204*	MB 207**	MB 208
Catalyst composition [F/Al ratio]	0.1	0.1	0.001	0
Pore volume [cm ³ /g]	0.4272	0.4052	0.5265	0.6292
Specific surface area [m ² /g]	246.8	58.9	41.9	272.0
Mean pore radius [nm]	3.5	6.0	13.0	6.7

* Physical analyses after reaction: T = 200°C, C₂H₂/N₂ = 0.1, τ = 2s

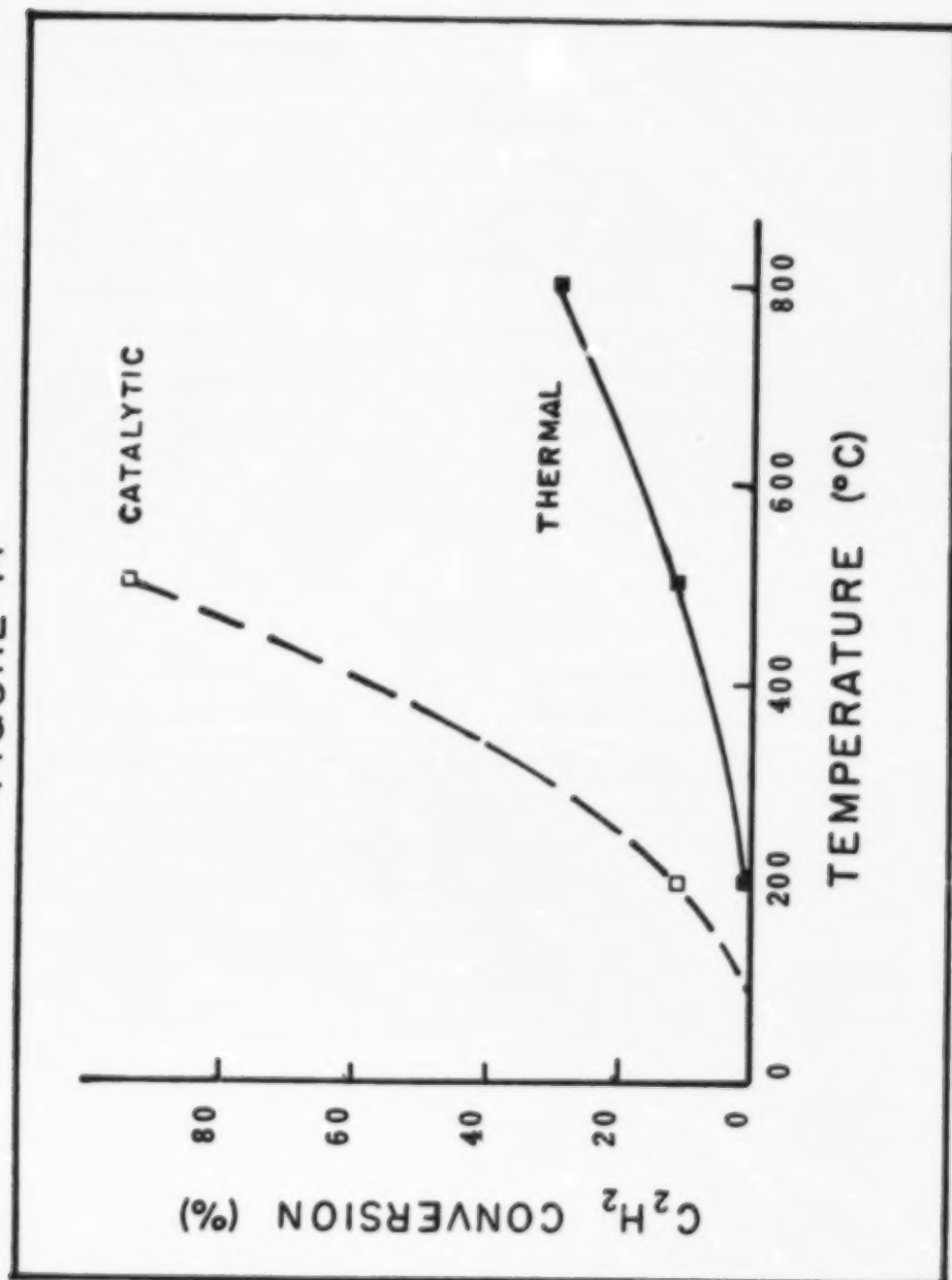
** Ratio of F/Al = 0.1 upon preparation, after calcination however, ESCA revealed F/Al < 0.001

Acetylene conversion as a function of temperature is illustrated in Figure 14 for the thermal reaction and for a fluorinated alumina catalyst. The thermal reaction is negligible at 200°C. The effect of the catalyst is pronounced. Higher conversions can be achieved with this catalyst and at much lower temperatures. A simplified product distribution with a fluorinated alumina catalyst is given in Figure 15. The liquid product recovered constitutes one-third of the total reaction products.

The gas phase products were identified as ethylene, ethane and methane. No butenes or other C₄'s were found. Analysis of the liquid phase products showed the presence of benzene, toluene, naphthalene, and derivatives of benzene and naphthalene as well as significant quantities of indene.

Acetylene conversion as a function of time on stream is illustrated in Figure 16 for several alumina catalysts. Both the alumina and the fluorided alumina catalyst calcined at 450°C exhibited high initial activities. The alumina catalyst however deactivated rapidly after only 90 minutes time on stream. The presence of fluorine (F/Al = 1/10) has contributed to a small reduction in surface area (247 vs 272 m²/g) of the original support. This catalyst nevertheless showed very high activity over a significantly longer period (240 min). A pronounced reduction in surface area was evidenced upon calcination of the fluorided alumina catalyst at 1000°C. ESCA analysis of this sample after calcination at this temperature revealed that little fluorine (<0.1 At %) was present in the catalyst (bulk or surface). The low surface area alumina exhibited very low activity. The importance of catalyst characterization in this study has been demonstrated.

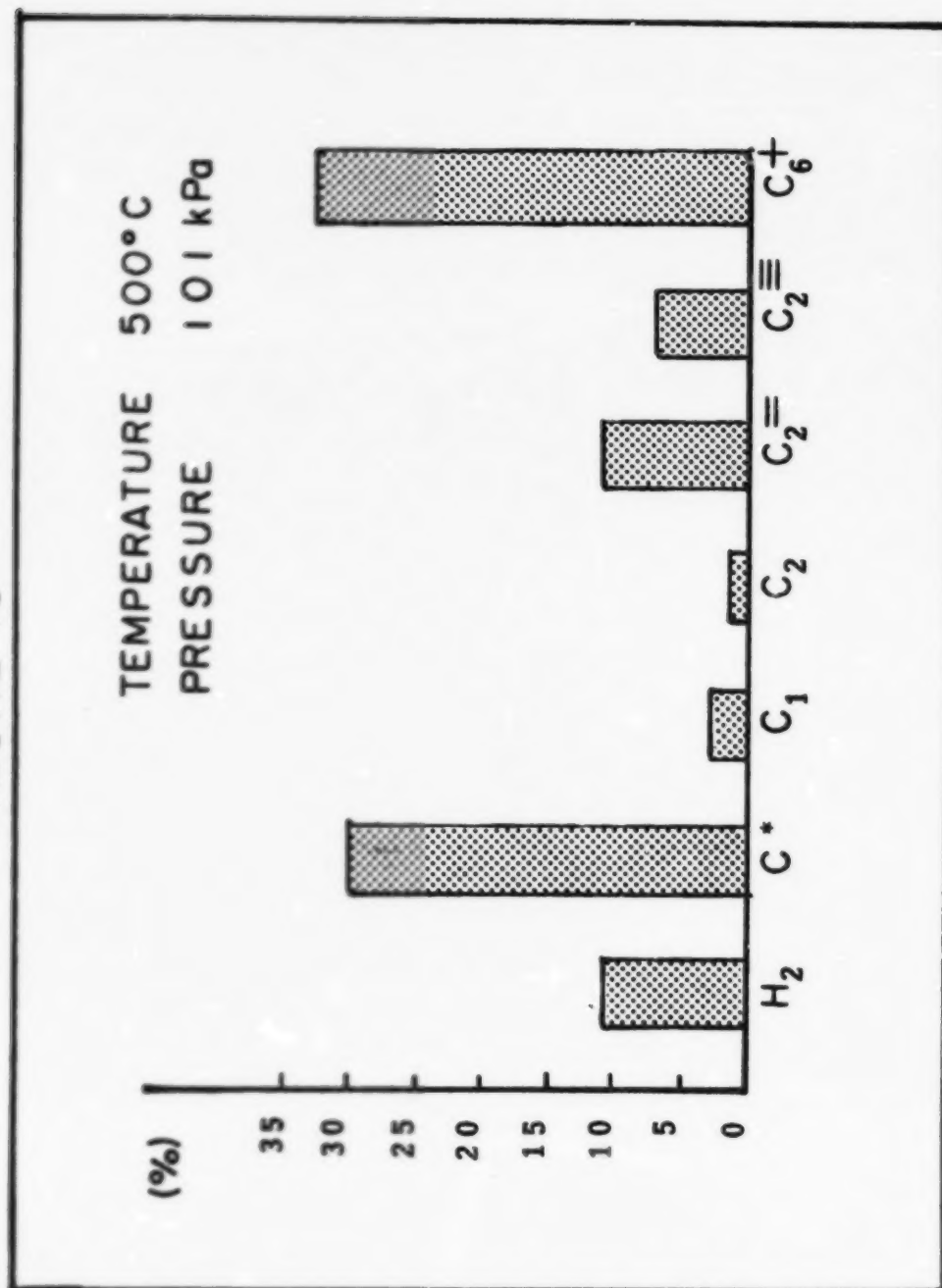
FIGURE 14



ACETYLENE CONVERSION AS A FUNCTION OF TEMP

$C_2H_2 : N_2 / 1 : 10$ $\tau = 2 s$

FIGURE 15



PERCENT BY WEIGHT OF ACETYLENE CONVERTED
TO PRODUCTS (HYDROGEN, CATALYST DEPOSIT,
CH₄, C₂H₆, C₂H₄, C₂H₂, LIQUIDS)

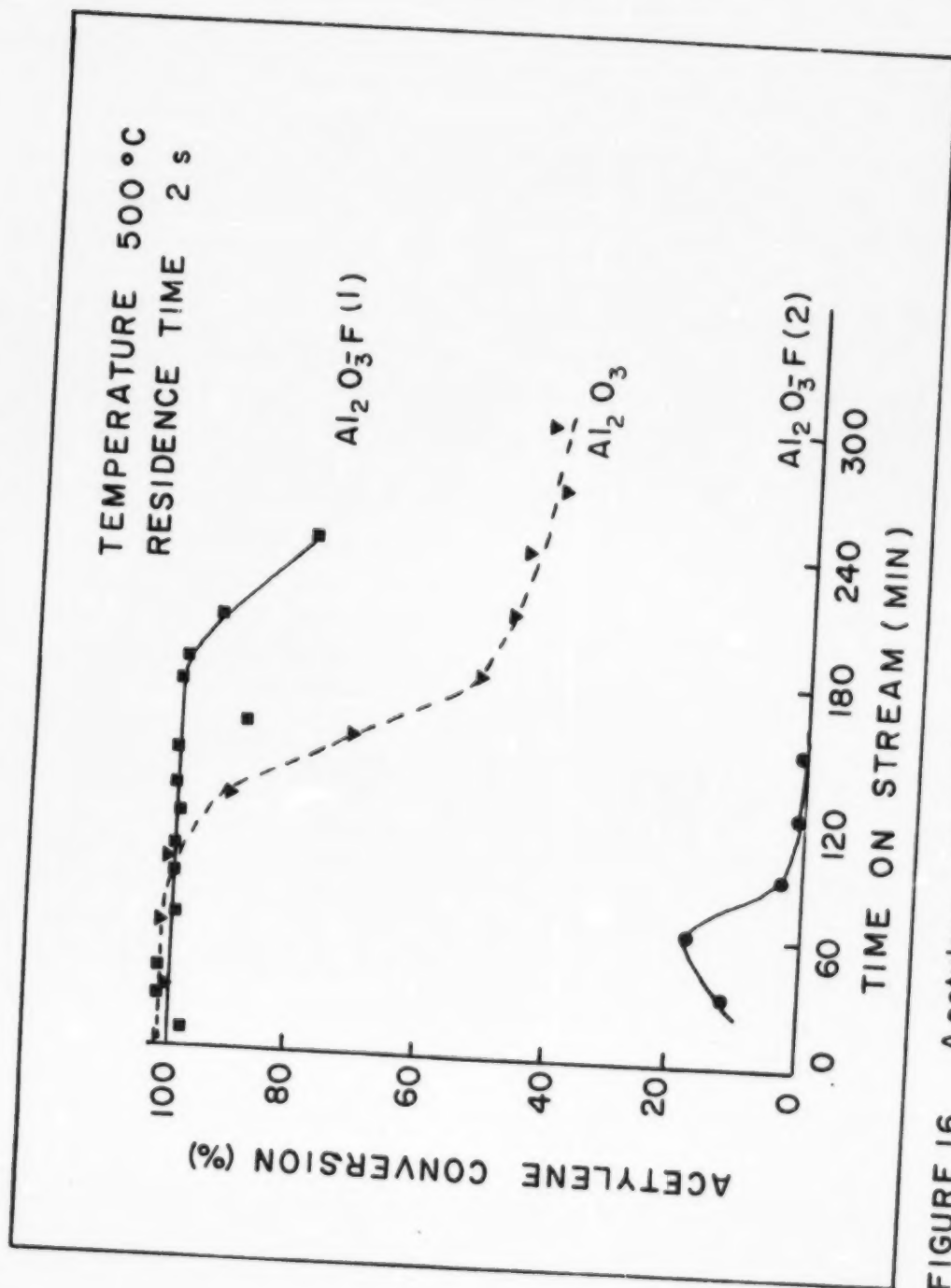


FIGURE 16 Acetylene conversion as a function of time on stream for Al_2O_3 and F impregnated alumina calcined at 450°C (1) and 1000°C (2)

REFERENCES

1. Canada. NEB. Canadian Energy: Supply and Demand 1980-2000, Ottawa, NEB, 1981.
2. Deckwer, W.D., Oil & Gas J Nov. 10, 198-213; 1980.
3. Eisenlohr, K.H. and Gaensslen, H. "Motor fuels from coal technology and economics"; Fuel Processing Technology 4:43-61; 1981.
4. Pinto, A. and Rogerson, P.L. "Impact of high fuel cost on plant design"; Chem Eng 84:102-108; 1977.
5. U.S. Patent 2.608,594 (Robinson).
6. U.S. Patent 3.176,045 (Jenny).
7. Back, M.H. and Back, R.A. "Thermal decomposition of methane"; in Pyrolysis Theory and Industrial Practice Albright, Crynes and Corcoran (eds.); Academic Press; 1983.
8. Miller, S.A., Acetylene, Its Properties, Manufacture and Uses; Vol 1 & 2; Ernest Benn Ltd.; London, 1965.
9. Tedeschi, R.J., Acetylene Based Chemicals from Coal and other Natural Resources; Marcel Dekker Inc.; 1982.
10. Leutner, H.W. and Stokes, C.S. "Producing acetylene in a plasma jet"; Ind & Eng Chem 53:5; 341-2; 1961.
11. Gladisch, H. "How Huels makes acetylene by DC arc"; Hydro Proc Petrol Ref 6:6; 159-164; 1962.
12. Hydro Proc Petrol Ref 42:11:129-240; 1963.
13. Cooke, N.E. et al. "Gasoline and hydrocarbon products from natural gas", presented at CAN-AM Congress, Montreal, Québec June 3-6, 1984.
14. Egloff, G., J Phys Chem 36:1457; 1932.
15. Meyer, R., Ber 45:1609; 1912.
16. Reikhsfel'd, V.O. and Makovetskii, K.L. "The cyclization of alkynes and their derivatives"; Russian Chemical Reviews 34:7:510-523; 1966.
17. Chem Eng 75:9:67; 1968.
18. Roginskii, S.Z., in A.A. Baladin et al. (eds.): Scientific Selection of Catalysts. KeterPubHouse; Kiryat Moshe, English translation, 1968.
19. Satterfield, C.N., Heterogeneous Catalysis in Practice; McGraw-Hill Book Co.; 1980.
20. Bond, G.C., Catalysis by Metals; Academic Press; London; 1962.

21. Bond, G.C. and Wells, P.B. "The hydrogenation of acetylene", Part I; J of Catal 4:211-219; 1965. Part II; J of Catal 5:65-73; 1965. Part III; J of Catal 5: 419-427; 1966.
22. Sheridan, J. "The metal-catalysed reaction between acetylene and hydrogen" Part II; J Chem Soc 133-142; 1945. Part III; J Chem Soc 301-304; 1945. Part IV; J Chem Soc 305-311; 1945. Part V; J Chem Soc 470-476; 1945. Part VI; J Chem Soc 2962-2966; 1952.
23. Moses, J.M. et al. "The effect of catalyst treatment on the selective hydrogenation of acetylene over palladium/alumina"; J Catal 86:417-426; 1984.
24. Sarkany, A. et al. "Green oil poisoning of a Pd/Al₂O₃ acetylene hydrogenation catalyst"; Applied Catalysis 12:3; 1984.
25. Sarkany, A. and Gucci, L. "On the aging phenomenon in palladium catalyzed acetylene hydrogenation"; Applied Catalysis 10:369-388; 1984.
26. McGown, W.T. et al. "Hydrogenation of acetylene in excess ethylene on an alumina-supported palladium catalyst at atmospheric pressure in a spinning basket reactor"; J Catal 51:173-184; 1978.
27. Kranich, W.L. et al. "Acetylene hydrogenation using palladium zeolite catalysts", Applied Catalysis 13:257-267; 1985.
28. Back, M., "Mechanism of the pyrolysis of acetylene"; Can J Chem 49:2199-2204; 1971.
29. Kesmodel, L.L. et al. "LEED analysis of acetylene and ethylene chemisorption on the Pt Surface: evidence for ethynidyne formation"; J Chem Phys 70:05:2180-2188; 1979.
30. Al-Ammar, A. and Webb, G. "Hydrogenation of acetylene over supported metal catalysts"; J.C.S. Faraday Trans 74:195 and 657; 1978.
31. Wender, I. and Pino, P. (eds). Organic Synthesis via Metal Carbonyls; Vol. 1, Interscience Publishers.
32. Nelson, W.L. Petroleum Refinery Engineering, 3rd Ed; McGraw-Hill Book Co.; 1949.
33. Pines, H., The Chemistry of Catalytic Hydrocarbon Conversions, Academic Press; 1981.
34. Goldstein, M. in Experimental Methods in Catalytic Research R.B. Anderson, (ed.) Academic Press, 1968.
35. Bashin, M.M. et al. "Infrared study of the effect of surface hydration on the nature of acetylenes adsorbed on α -alumina"; J Phys Chem 74:22:3973-3980; 1970.
36. Yates, D.J.C. and Lucchesi, P.J. "Infrared spectra of acetylene and acetylene derivatives adsorbed on alumina and silica"; J Chem Phys 35:1:243-255; 1961.

37. Sheppard, N. and Yates, D.J.C. "Changes in infrared spectra of molecules due to physical adsorption"; Proc Roy Soc A 238:69-88; 1957.
38. The Tam, N. et al. "Vibrational spectra of molecules on zeolites"; J Chem Soc Faraday Transactions I 72:2577-2597; 1976.
39. Heaviside, J. et al. "Adsorption and polymerization of acetylene on oxide surfaces - Raman Study"; J Chem Soc Faraday Transactions I 74:2542-2549; 1978.
40. Elev, I.V. et al. "Cyclotrimerization of acetylene on Ni^{2+}/SiO_2 thermally reduced and photoreduced by hydrogen"; Kinetics and Catalysis 24:4:2:797-799; 1983.
41. Pichat, P. et al. "Spectroscopic study of cyclotrimerization of acetylene on NiY zeolites. Influence of the location of the Ni^{2+} ions"; J Catal 32: 190-203; 1974.
42. Massimila, L. et al., Chim e Ind 44:341; 1962.
43. L  glise, J. et al. "Cyclotrim  risation de l'ac  tyl  ne catalys  e par les z  olithes Y chrom  es"; Comptes Rendus des S  ances Acad Sci, Ser C 291:2:41-4; 1980.
44. L  glise, J. et al. "Acetylene condensation catalyzed by CrY zeolites: formation of alkylaromatics"; Catalysis by Zeolites 95-202; 1980.
45. Tsai, P. and Anderson, J.R. "Reaction of acetylene over ZSM-5 type catalysts"; J Catal 80:207-214; 1983.
46. Berak, J.M. et al. "Properties of ZSM-5 type zeolites related to the SiO_2/Al_2O_3 ratio"; React Kinet Catal Lett 25:3,4:323-327; 1984.
47. U.S. Patent 4,424,401 (White et al., Jan. 3 1984).
48. Rabo, J.A., Zeolite Chemistry and Catalysis ACS Monograph 171; 1976.
49. Breck, D.W., Zeolite Molecular Sieves; John Wiley & Sons, N.Y.; 1974.
50. Gatz, B. et al., Chemistry of Catalytic Process; McGraw-Hill Book Co.; 1975.
51. Derouane, E.G. "New aspects of molecular shape-selectivity: Catalysis by ZSM-5"; Catalysis by Zeolites, B. Imelik et al., (eds), Elsevier Pub. Co., Amsterdam, 1980.
52. Sckokart, P.O. et al. "The chemistry and surface chemistry of fluorinated alumina"; J Colloid Interface Sci 70:2:209-222; 1979.
53. Choudhary, V.R. "Fluorine promoted catalysts: activity and surface properties"; Ind Eng Chem Prod Res Dev 16:1:12-22; 1977.
54. Covini, R. et al. "Acidity of fluorinated aluminas, and their catalytic activity in cumene hydrodealkylation", J Catal 7:126-134; 1967.

55. Tanaka, K. and Ozaki, A. "Acid-base properties and catalytic activity of solid surfaces"; J Catal 8:1-7; 1967.
56. Shibata, K. et al. "Acidic properties of binary metal oxides"; Bull Chem Soc Japan 46:10:2985-2988; 1973.
57. Tanabe, K. et al. "A new hypothesis regarding the surface acidity of binary metal oxides"; Bull Chem Soc Japan 47:5:1064-1066; 1974.
58. Gishti, K. et al. "On the role of phosphate anion in the $\text{MoO}_3\text{-Al}_2\text{O}_3$ based catalysts"; Applied Catalysis 12:381-393; 1984.
59. Chadwick, D. et al. "Influence of phosphorus on the HDS activity of Ni-Mo/8-- Al_2O_3 catalysts"; Preparation of Catalysts III, Elsevier Science Publishers, B.V. Amsterdam, 323-332; 1983.
60. Miranda, R. et al. "Catalytic conversion of alcohols: role of sodium in altering the alkene products obtained with alumina catalysts"; J Catal 88:542-545; 1984.
61. Fraissard, J. "Why are HY zeolites so much more active than amorphous silica-alumina"; Catalysis by Zeolites, B. Imelik et al., (eds.), Elsevier Pub. Co., Amsterdam, 1980.
62. Scherzer, J. "The preparation and characterization of aluminum deficient zeolites"; Catalytic Materials Relationship Between Structure and Reactivity (eds) T.E. Whyte (Jr.), R.A. Dalla Betta, E.G. Derouane, R.T.K. Baker. ACS Symposium Series No 248: 157-199; 1983.
63. Wojciechowski, B.W. "The kinetic foundations and the practical application of the time on stream theory of catalyst decay"; Cat Rev Sci Eng 9:1:79-114; 1974.
64. Poncelet, G. and Grange P.V., Studies in surface science and catalysis 16 Preparation of Catalysts Vol. III, Elsevier, Amsterdam, 1983.
65. Kotanigawa, T. et al. "The influence of preparation methods on the pore structure of alumina"; Applied Catalysis 1:185-200; 1981.
66. Vedrine, J.C. et al. "Combined physical techniques in the characterization of Zeolite ZSM-5 and ZSM-11 acidity and basicity"; Catalytic Materials Relationship Between Structure and Reactivity (eds) T.E. Whyte (Jr.), R.A. Dalla Betta, E.G. Derouane, R.T.K. Baker. ACS Symposium Series No 248: 253-273; 1983.
67. Allenger, V.M. et al. "Conversion of acetylene to liquid fuel"; 34th Canadian Chemical Engineering Conf. Proc. Québec, 135-137; 1984.
68. Allenger, V.M. "Natural gas to liquid fuels via acetylene"; Division Report ERP/ERL 84-73(1R); CANMET, Energy, Mines and Resources, Canada, 1984.
69. Zelinsky, N.D., Ber 57:264; 1924.

70. Kovache, A. and Tricot, E., Chim et Ind 13:361-537; 1925.
71. Ika and Ogura, J Soc Chem Ind Japan 31:78-86; 1928.
72. Fujio, C., J Soc Chem Ind Japan 31:78-86; 1928.
73. Fischer, F. et al., Brennstoff - Chem 10:279; 1929.
74. Hague, E.N. and Wheeler, R.V., J Chem Soc 391; 1929.
75. Berl, E. and Hofmann, K.N., Z Agnew Chem 44:259; 1931.
76. Schwarz, R. and Bessel, G., Ber 77B:512-515; 1944.
77. Cadariu, I., An Acad RSR Filiula Cluj 3:4:77-94; 1954.
78. Cullis, C.F. et al., Trans Far Soc 58:1117-1127; 1962.
ibid. 59:361-368; 1963.
79. Chang-Li, S., Chemistry (TAIPEI) 1:1-14; 1963.

APPENDIX A

```
20 REM
30 REM program calculates free energy of formation of hydrocarbons
40 REM
50 REM heat capacity of hydrocarbon gases expressed in the form
60 REM  $A + B T + C T^2 + D T^3$ 
70 REM
80 REM heat capacity of hydrogen expressed in the form
90 REM  $A + B T$ 
95 IF N$='*' GO TO 150
100 REM
110 REM heat capacity of carbon (Graphite) expressed in the form
120 REM  $A + B T + C / T^2 + D / T^3$ 
130 REM
140 REM
150 READ R
160 DATA 1.987
170 READ C1, C2, C3, C4
180 DATA 5.32692, 3.6954E-04, -7.35084E05, 1.2954E08
190 READ H1, H2
200 DATA 6.62, 8.1E-04
210 OPEN 'SY1:HEAT.DAT' FOR INPUT AS FILE #5
220 OPEN 'LP:' FOR OUTPUT AS FILE K#6
240 INPUT #5, N$
245 IF N$='*' GO TO 9999
250 INPUT #5, P, H, C
260 INPUT #5, P1, P2, P3, P4
265 INPUT #5, H0, G0
280 PRINT #6, N$
290 PRINT #6, P1, P2, P3, P4
300 PRINT #6
310 PRINT #6, ' T          -LN K          K          DEL G'
320 REM
330 REM
340 REM
350 REM calculating the integration constants
360 REM
370 LET T2=298.2
380 LET T3=T2*298
390 LET L=LOG (298)
400 I1 = P1*298+P2*T2/2+P3*T3/3+P4*T2*T2/4
410 I2 = H1*298+H2*T2/2
420 I3 = C1*298+C2*T2/2-C3/298-C4/2/T2
430 I4 = -H0/298
440 I4 = I4+P*(P1*L+P2*298/2+P3*T2/6+P4*T3/12+T1/298)
450 I4 = I4-H*(H1*L+H2*298/2+I2/298)
460 I4 = I4-C*(C1*L+C2*298/2+C3/T2/2+C4/T3/6+I3/298)
470 REM
480 REM
490 T=300
```

```
500 REM
510 REM
550 REM calculating the equilibrium constant
560 L1=LOG(T)
570 T5=T*T
580 T6=T5*T
590 T7=T/2
600 K1=-H0/T
610 K1=K1+P*(P1*L1+P2*T7+P3*T5/6+P4*T6/12+I1/T)
620 K1=K1-H*(H1*L1+H2*T7+I2/T)
630 K1=K1-C*(C1*L1+C2*T7+C3/T5/2+C4/T6/6+I3/T)
640 K1=K1-I4
650 REM
660 REM calculating the equilibrium constant
670 REM
680 K=EXP (K1/R-G0/R/298)
685 K2=-LOG(K)
690 REM
700 REM calculating the free energy of reaction
710 G=R*T*K2
720 IF T 2500 THEN GO TO 9998
730 PRINT #6,T,K2,K,G
740 T=T+100
750 GO TO 560
760 REM
770 REM
780 REM
790 REM
9998 GO TO 240
9999 END
```

APPENDIX B

ANALYTICAL CRITERIA FOR TEMPERATURE GRADIENTS

TEMPERATURE GRADIENT IN A CATALYST PELLET

The magnitude of the temperature difference inside a particle (without further complications of external mass and heat transfer resistances) was originally derived by Damköhler. The derivation based on simultaneous solution of heat and mass balances for a particle of any geometry can be found in Levenspiel, Chemical Reaction Engineering, 2nd Ed. The temperature difference ΔT_p is given by:

$$\Delta T_p = T_s - T_s^s = \frac{D_{eff} \cdot (C_s^s - C_s) \cdot (-\Delta H_r)}{k_{eff}}$$

where T_s = absolute temperature at centre of porous particle

T_s^s = absolute temperature at surface of porous particle

C_s = concentration of reactant at centre of porous particle

C_s^s = concentration of reactant at surface of porous particle

ΔT_p = temperature variation within catalyst pellet

D_{eff} = effective mass diffusivity

$-\Delta H_r$ = heat of reaction

k_{eff} = effective thermal conductivity

It can be seen that the maximum gradient, ΔT (MAX) occurs for complete reaction, $C_s = 0$, so that

$$\Delta T_p = T_s^s - T_s = \frac{(-\Delta H_r) \cdot D_{eff} \cdot C_s^s}{k_{eff}}$$

k_{eff}

The result holds for a particle of any geometry under steady-state conditions. The temperature gradient is therefore dependent on the heat of reaction, the transport properties of the particle, and the surface concentration of reactant.

Assuming the reaction $C_2H_2 \rightarrow \text{PRODUCTS}$ is first order and that $\Delta H_r = -50$ kcal/mol C_2H_2 ($T = 200^\circ\text{C}$, 100 kPa), $C_s^s = yP/RT = 3.6 \times 10^{-3}$ mol C_2H_2/L , $D_{eff} = 29.3 \times 10^{-3}$ cm²/s, $k_{eff} = 5.24 \times 10^{-4}$ cal/cm·s·K, then a $\Delta T_p = 10$ K is expected inside the particle.

TEMPERATURE GRADIENT IN THE FILM SURROUNDING THE PELLET

The temperature gradient in the film can be evaluated by equating the rate of heat removal through the film with the rate of heat generation within the pellet. Thus:

$$\Delta T_f = \frac{L \cdot (-r_a) \cdot (-\Delta H_r)}{h}$$

where ΔT_f = temperature variation across gas film

$L = R_p/3$ = effective length

$-r_a$ = reaction rate

h = heat transfer coefficient obtained from empirical correlations

APPENDIX C

SAMPLE BINARY OXIDE ACIDITY CALCULATIONS

Consider the structure of $\text{Al}_2\text{O}_3 [\text{SiO}_2]$ where Al_2O_3 is the major component oxide. In this structure, the coordination numbers of the positive elements in the component single oxides remain 6 for Al and 4 for Si when they are mixed whereas those of the negative elements should be 4 in $\text{Al}_2\text{O}_3 [\text{SiO}_2]$ according to postulates 1 and 2 (57). The 4 positive charges of the Si atom are distributed to 4 bonds, i.e., 1 positive charge is distributed to each bond, while -2 charges of the oxygen atom are distributed to 4 bonds, i.e., -1/2 of a valence unit is distributed to each bond. The difference in charge for 1 bond is 1/2, i.e., 1-1/2 and for all the bonds the valence unit of 4 (+1/2) is in excess. According to this picture, the Lewis acidity is assumed to appear as a consequence of the excess positive charge.

Table C1 - Valence and coordination number of some compounds

Compound	Valence	Coordination Number	
		+ charge	-charge
Al_2O_3	+3	6	4
MgO	+2	6	6
TiO_2	+4	6	3
SiO_2	+4	4	2
P_2O_5	+5	6	4

As acidity is characterized as a tendency to attract electrons to form a covalent bond, the acidity of a metal ion according to the Lewis concept may increase with its electron-withdrawing power or electronegativity. The generalized electronegativity of the metal ion (X_i) is defined as:

$$X_i = (1 + 2Z) X_0$$

where Z is the valence of the metal ion and X_0 is the electronegativity of the neutral atom ($Z=0$) given by Pauling. Table C2 lists the X_i factor for some metal ions. This factor has been correlated with acidity (55-57).

Table C2 - Electronegativity factor for some metal ions

METAL ION	ELECTRONEGATIVITY	CHARGE	X_i FACTOR
Na	0.9	+1	2.7
Mg	1.2	+2	6
Al	1.5	+3	10.5
Si	1.8	+4	16.2
P	2.1	+5	23.1
Ti	1.5	+4	13.5

APPENDIX D

PRESSURE DROP CALCULATION

Nitrogen flowrate (NTP) = 250 mL/min

Acetylene flowrate (NTP) = 25 mL/min

Total reactant gas flowrate = 275 mL/min

Reactor configuration

Length = 55 cm

Catalyst bed = 12.5 cm

Internal diameter = 1.0 cm; thermowell O.D. = 0.3175 cm

Particle size = 0.5 - 1 mm

Reynolds number calculation

$$Re = \frac{\rho D_p U_m}{\mu}$$

where D_p = particle diameter
 U_m = superficial velocity
 μ = viscosity
 ρ = gas density

At 500°C, 6 psig the total volumetric flowrate (v_0) is given by

$$v_0 = 275 \frac{\text{mL}}{\text{min}} \cdot \frac{[273 + 500]}{298} \cdot \frac{[14.7]}{[14.7 + 6]}$$

$$= 506.6 \frac{\text{mL}}{\text{min}}$$

The superficial velocity, (U_m), is given by v_0/A where A is the cross-sectional area of the annular catalyst bed

$$U_m = \frac{v_0}{\pi/4(d_i^2 - d_t^2)} = \frac{506.6}{\pi/4(1^2 - .3175^2)} = 717 \frac{\text{cm}}{\text{min}}$$

The density of nitrogen can be calculated from:

$$\rho(500^\circ\text{C}) = \frac{(14.7 + 6)(28)}{(82.06)(773)} = 6.21 \times 10^{-4} \frac{\text{g}}{\text{mL}}$$

The viscosity of nitrogen at 500°C is .036 centipoise or $3.6 \times 10^{-4} \text{ g cm}^{-1} \text{ s}^{-1}$. (Perry's Handbook, 5th Ed.)

The Reynolds number can now be calculated

$$Re = \frac{(6.21 \times 10^{-4}) (0.05) (12)}{3.6 \times 10^{-4}}$$

$$Re = 1.04$$

The pressure drop parameter is 1500 at this Reynolds number. (Perry Handbook, 5th edition).

$$\frac{P \cdot g_c \cdot D_p^2}{L \cdot \mu \cdot U_m} = 1500$$

$$P = \frac{1500 L \mu U_m}{g_c D_p^2}$$

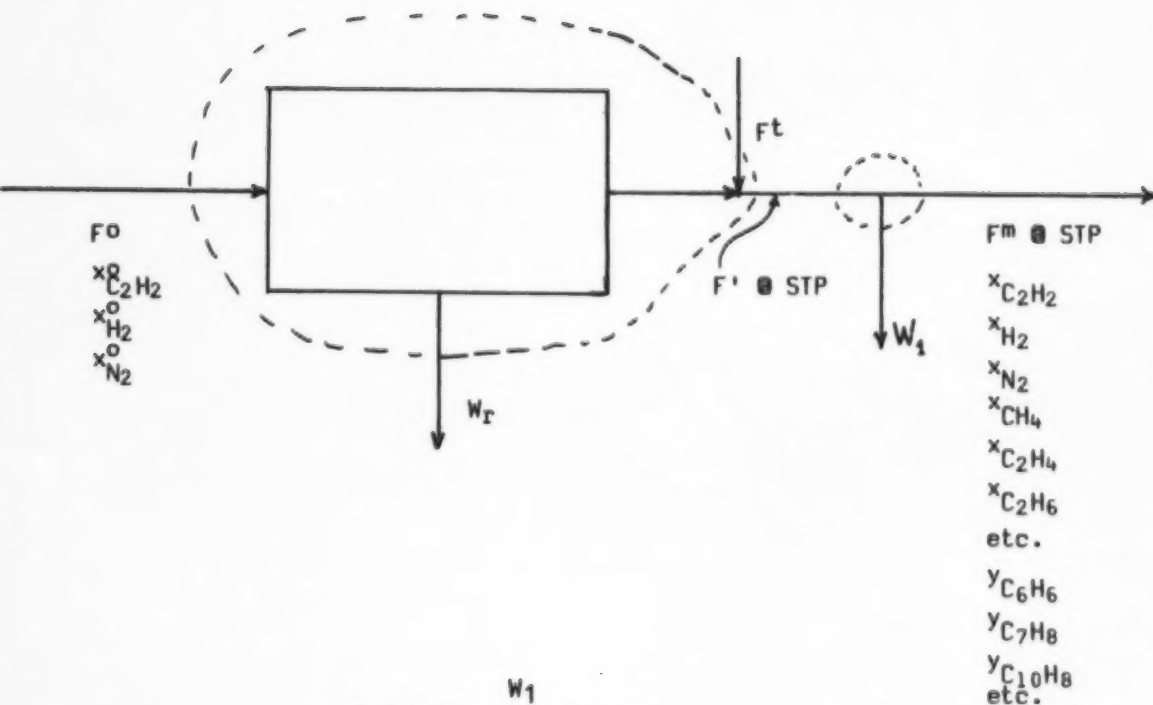
$$= \frac{1500 [55(1/2.54) (1/12)] [.036(6.72 \times 10^{-4})] [12(1/2.54)(1/12)]}{32.2 \left\{ \frac{\text{lbm ft}}{\text{lb f s}^2} \right\} \left\{ \frac{0.05 \text{ cm}^2}{2.54 \cdot 12} \right\}}$$

$$= 298 \frac{\text{lb f}}{\text{ft}^2}$$

$$P = 2.1 \text{ psi} = 14.5 \text{ kPa}$$

APPENDIX E

DATA ANALYSIS



$$F' = F^m + \frac{W_1}{\rho \cdot t} = F^m$$

- where W_1 = weight of the condensed liquid (g)
 ρ = density of the condensed liquid (g/mL)
 t = length of the experimental run (min)
 F_0 = feed flowrate (mL/min)
 F^m = product gas flowrate without condensibles (mL/min)
 W_r = weight of the carbonaceous residue (g)
 F_t = flowrate of the liquid tracer (mL/min)
 x^0, x' = mole fraction of the components in the feed and product respectively
 y' = mole fraction of the liquid vapor in the product stream

CALCULATIONS FOR THERMAL CONDUCTIVITY DETECTOR ANALYSES

Calculating Response Factors

$$RF(i) = \frac{CONC(i) * AREA(R)}{AREA(i) * CONC(R)}$$

where:

- RF(i) = response factor for component i
- CONC(i) = amount of component i in the calibration sample
- AREA(i) = area of the component i peak
- CONC(R) = amount in the calibration sample of the component (identified IP)
- AREA(R) = area of the IP component peak

$$CONC(i) = \frac{RF(i) * AREA(i)}{\sum_{i=1}^n RF(i) * AREA(i)} * XF$$

- CONC(i) = percentage of component i present in the analysis sample
- RF(i) = response factor for component i calculated in the calibration run
- AREA(i) = the area of the component i peak measured in the analysis run
- XF = total percentage of the analysis sample represented by the components integrated in the chromatogram, if other than 100.
- $\sum_{i=1}^n RF(i) * AREA(i)$ = summation of all of the detector response connected areas in the chromatogram.

CALCULATIONS FOR FLAME IONIZATION DETECTOR ANALYSES

Calibration for each component of interest i:

$$RF(i) = \frac{CONC(i)}{AREA(i)} \frac{AREA(is)}{CONC(is)}$$

where:

RF(i) = response factor for component i

CONC(i) = amount of component i used in the calibration sample

AREA(i) = area of the component i peak

AREA(is) = area of the internal standard peak

CONC(is) = amount of the internal standard used in the calibration sample

Analysis of each component of interest:

$$CONC(i) = \frac{IS}{SA} \frac{RF(i) AREA(i)}{RF(is) AREA(is)} XF$$

where:

CONC(i) = amount of component i present in the analysis sample.
(If this value is desired as a percentage, XF = 100)

IS = amount of internal standard added to the analysis samples

SA = amount of sample material measured

RF(i) = response factor of component i determined by calibration

AREA(i) = area of the component i peak in the analysis run

RF(is) = response factor of the internal standard is 1, by definition

AREA(is) = area of the internal standard peak in the analysis run

XF = a scaling factor which may be used as a conversion factor.
If the CONC(i) is desired as a percentage, XF must equal 100,
otherwise, its use is optional

To obtain quantitative results from the GC trace, it is necessary to use correction factors. The amount of the correction is a function of the response of a given compound to the detector. Relative sensitivity values for the FID detector are given by Dietz(A1). Each area is divided by the relative sensitivity to get true area. Normalizing the results gives weight per cent of each component. For hydrocarbons with three exceptions, the values are all approximately 1.0. The three exceptions are benzene 1.12 and toluene 1.07 and acetylene 1.07.

(A1) Dietz, J.H., J. Gas Chromatography 5:68; 1967.

ANALYSIS

Tracer sample size: 1 mL loop

Tracer flowrate: F_t mL/min

Gas flowrate: $F'' = F' \text{ mL/min} \frac{T + 273}{273} \frac{14.7}{14.7 + P}$ at reaction conditions

Residence time in loop: $1 \text{ mL}/F'' = \tau \text{ min}$

In τ minutes, $(F_t \tau)$ mL of tracer will be in the loop,
or $(\rho_t F_t \tau)$ g of tracer will be in the loop.

moles of tracer in sample loop $n_{is} = \frac{\rho_t F_t \tau}{M_t}$ where M_t = molecular weight of the tracer

Now, to obtain SA, use the ideal gas law, $n = PV/RT$, where $V/R = 1.219 \times 10^{-2}$

moles of sample in sample loop $n_{sa} = \frac{1.219 \times 10^{-2} P_{abs}}{(273 + T)}$

and the $\text{CONC}(i) = (n_{is}/n_{sa}) (\text{area}_i/\text{area}_{is})$ (mol %)

Now, the molar flowrate of a component is given by:

$$C(i) = \frac{\text{Conc}(i)}{22,400 \text{ mL/mol}} \frac{F'}{\text{min}} \text{ @ STP}$$

REACTANT FLOWRATE

$$F^0 = F_{N_2}^0 + F_{C_2H_2}^0 + F_{H_2}^0$$

TIE COMPONENT BALANCE

$$F^m = x_{N_2}^0 F^0 / x_{N_2}^1$$

ACETYLENE CONVERSION

$$x = \frac{x_{C_2H_2}^0 F^0 - x_{C_2H_2}^1 F^m}{x_{C_2H_2}^0 F^0}$$

TOTAL MASS BALANCE

$$\text{moles/min of } N_2 = x_{N_2}^1 F^m / 22,400$$

$$H_2 = x_{H_2}^1 F^m / 22,400$$

$$C_2H_2 = x_{C_2H_2}^1 F^m / 22,400$$

•
• etc for C_2H_4 , C_3H_4 , C_3H_6
•

$$\text{moles/min of } C_6H_6 = y_{C_6H_6}^1 F^1 / 22,400$$

$$C_7H_8 = y_{C_7H_8}^1 F^1 / 22,400$$

•
• etc for other liquid components
•

INPUT

$$F^0 (x_{N_2}^0 M_{N_2} + x_{C_2H_2}^0 M_{C_2H_2} + x_{H_2}^0 M_{H_2}) / 22,400 + F^t \rho^t$$

OUTPUT

$$F^m (x_{N_2}^1 M_{N_2} + x_{H_2}^1 M_{H_2} + x_{C_2H_2}^1 M_{C_2H_2} + x_{C_2H_4}^1 M_{C_2H_4} + \dots) / 22,400 +$$

$$\text{OUTPUT} \quad F' (Y_{C_6H_6}^{'} M_{C_6H_6} + Y_{C_7H_8}^{'} M_{C_7H_8} + \text{etc}) / 22,400 + W_r$$

where W_r is the carbonaceous deposit on the catalyst.